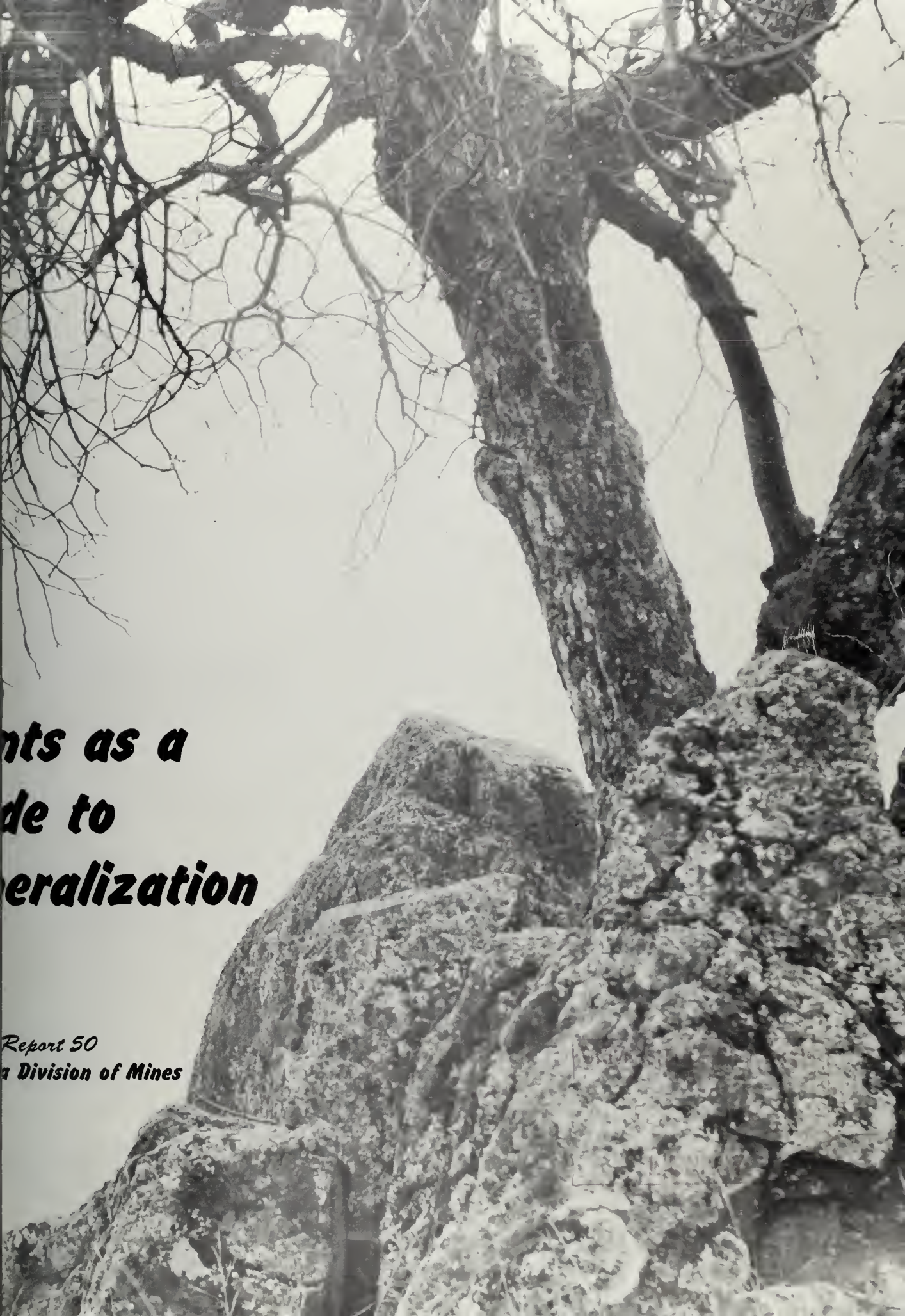

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Report 50
a Division of Mines

SHOUT
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IT

COVER—Silhouette of an oak tree in the California Mother Lode. *Photo by Mary Hill.*

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DEPARTMENT OF NATURAL RESOURCES
DeWITT NELSON, Director

DIVISION OF MINES
FERRY BUILDING, SAN FRANCISCO 11
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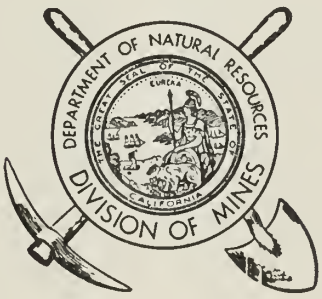
N FRANCISCO SPECIAL REPORT 50 1958

PLANTS AS A GUIDE TO MINERALIZATION

By DONALD CARLISLE and GEORGE B. CLEVELAND



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PLANTS AS GUIDE TO MINERALIZATION †

By Donald Carlisle * and George B. Cleveland **

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ABSTRACT

buried ore deposit may provide to the soil above a abnormal amount of the metal or metals it contains; urn, the soil may provide a large amount of the same als to the plant cover. The ore deposit may therefore, er favorable conditions, be detected by the abnor- ly high concentration of these metals in the plants, by the distribution of plants that will or will not rate certain metals more readily than others. If the nts are systematically collected and carefully ana- d, the results may indicate the possibility of a buried deposit. This technique of sampling, analyzing, and rpreting the plant cover is called biogeochemical specting.

lthough the method has the advantage of rapidity is relatively inexpensive, the numerous factors (such ge and organ of the plant, soil pH, geochemistry of and its exchange capacity) that bear on the concen- ion of metals within plants must be considered. onomists and other research workers have provided e data; biogeochemical field work has added more.

hree known molybdenum deposits in California were spected in the course of this study. At the Bour ybdenum mine, San Diego County, molybdenite is eminated as flakes in an aplite dike that cuts grano- diorite. Plants growing above the dike showed an abnormally high concentration of molybdenum; the soil in which they were rooted was also high in molybdenum, but not so anomalously as the plants.

Flakes of molybdenite were found in the Cosumnes mine, El Dorado County, along the contact of an igneous body and metasedimentary rocks of the Carboniferous (?) Calaveras group, though the mine itself was not primarily worked for molybdenum. Plant samples from the area showed the highest concentration of molybdenum to be over the contact zone, as geological field studies also indicated.

At the Tyler Creek tungsten mine, Tulare County, the analysis of samples collected along a fault zone that traversed several rock types indicated that the underlying rock type exercised some control over the molybdenum concentration. No definite pattern of mineralization could be determined from the plant analysis; higher values were seemingly distributed at random.

Several factors other than the metal content of the soil may influence the metal content of a plant. If these factors vary within the area of survey, and if they have a significant effect on metal uptake, the biogeochemical results are misleading. Soil moisture and drainage influence the availability of some metals although, in general, the influence of the physical properties of soil is probably not great. Even the amount of sunlight and shade has a slight effect for some plants. The largest effects, however, are associated with the chemical properties of the soil both as an influence on the metabolism of plants and as a control of the state of the metal in the soil, as most of the metal in the soil is present not in minerals or in solution but as ions sorbed or exchanged in the soil materials, especially on clay minerals and organic matter, or else as complex ions. Consequently, the ability of the plant to absorb metals is moderately to profoundly influenced by the kind and concentration of exchange materials, by the soil pH, by the kind and concentration of other ions, and by organic materials and micro-organisms. The exchange capacity of a soil also largely determines the amount of metal that will be taken and retained from various sources. Available data suggest that the clay or organic content of a soil can be responsible for variations of a few fold in the metal content of that soil.

BIOGEOCHEMICAL PROSPECTING

Biogeochemical prospecting, like most geochemical and geophysical methods of exploration, is an adjunct to other techniques for the discovery of economic mineral deposits. As with other geochemical and geophysical methods, clues to the location of hidden deposits are sought through relatively inexpensive procedures performed on readily accessible materials at the earth's surface. In biogeochemical prospecting the procedures are (1) the observation of the distribution of plants (indicator plants) that tolerate or fail to tolerate abnormally high concentrations of certain metals in the soil (this method is sometimes called botanical prospecting); or (2) the sampling and analysis of plants that concentrate or of plants that merely acquire certain metals

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ssociate Professor of Geology, University of California, Los Angeles.
eologist, California State Division of Mines.

FIGURE 1. Maps of California showing the close relationship between soil pH and amount of rainfall. *Modified from Jenny (1951).*

from the soil, (accumulator plants)* and (3) the interpretation of the data thus obtained. The basic assumptions, then, are that a high metal content in the soil may reflect a deposit of metal somewhere at depth and that the high metal content in the soil may be reflected in some way in the plants. Indicator plants, though of limited occurrence, are very useful when present and offer an extremely cheap method for reconnaissance of large areas to show variations in metal content of the soil. An example is the use of some species of *Astragalus, Stanleya,* and other selenium- and sulfur-tolerant plants in the search for uranium deposits (Cannon, 1952; Cannon and Starrett, 1956; Dorn, 1937; Lidgey, 1897; Hawkes, 1950). The second technique, systematic sampling and analysis of plants for their metal content is more widely applicable, though best suited to small areas. It is with this technique and some of the problems involved that this report is concerned. The term biogeochemical prospecting will be used for this second technique.

Unusually high concentrations of metal commonly do develop in the soil near ore deposits. For example, the metal in the soil may be the residuum of a metal deposit now eroded. Grains of a primary ore mineral may have persisted through the weathering process or may have been concentrated through removal of more easily weathered gangue minerals. Residual concentrations of cassiterite, gold, and other minerals are sometimes produced in this way. If the primary ore mineral weathers readily a secondary mineral such as azurite, malchite, cerrusite or garnierite may remain in the soil. Under still other circumstances only traces of the ore metal may remain as a contaminant but in concentrations sufficiently large to distinguish the soil from other soils nearby. Or the metal in the soil may have been introduced or dispersed either as solid mineral particles carried by water, wind, or ice, or as dissolved ions in ground waters. In this event the source of the metal might not be nearby but might nevertheless be discovered through careful study of the dispersion pattern pears also that metal ions are able to migrate s ward directly from hidden deposits by proces well understood. Presumably they travel in pa upward percolating ground water and in part fusion within ground water. Ion exchange an reactions with soil materials probably play a rol within the reach of plant roots, metals may be concentrated at the surface very effectively by themselves. Goldschmidt (1937, pp. 670-71) has out how absorption of metals by plant roots, tra tion to the upper organs of the plant, and return earth when leaves are shed or the plant dies tend centrate them in the upper layers of the soil.

Agronomists have long recognized the ability of to accumulate some metals from the soil, especiall metals useful or necessary to the plant and als ability to absorb other metals present in the so though these appear to serve no useful purpose plant. Probably every element could be found in if sensitive enough analytical techniques were use the synthetic element, plutonium, is absorbed and located within plants (Jacobson and Overstreet, In some cases an unusually large amount of a metal in the plant can be correlated with an un high concentration of the metal in the soil in wh plant is growing. The abnormal amounts of go copper reported in horsetails is a classic example analyses of many of the world's coals did m prompt an early interest in the relationship b plant cover and the subsurface geology. Milner reported vanadium from Scottish coal and gol coals at Cambria, Wyoming. Germanium has been in many of the world's coals by Goldschmidt (193 more recently by others (Stadnichenko et al., 195 work of Palmquist and Brundin reported by the S Prospecting Company in 1939 was among the first cal applications of biogeochemical principles. Th method was employed with some success by Rank the vicinity of the nickel ore deposits at Ne northern Finland (Rankama, 1940). The value geochemistry was demonstrated by many investiga Scandinavia and has been applied successfully i land, Greece, U. S. S. R., Spain, Australia, South Nigeria, Canada, Venezuela, Poland, Brazil, Ge and the United States.

Prospecting Procedure. The procedure for chemical prospecting in an area is as follows: samples are collected according to a grid patter intervals along traverses. The same species of pla same organ of the plant and if possible plants same age are sampled at each station. Some worke fer to use only twigs of the previous year's g others use only leaves. Sampling stations may be f feet to 1000 feet apart depending upon the expect of the target and the size of the area involved general practice to collect a compound sample fo station by gathering the leaves, twigs or whatever is sampled from two, three or four trees or plants ing within a radius of perhaps 5 to 25 feet of the s All sampling is done within a single day or a fe

Where no single plant species grows over the area some workers have sampled two kinds of pl

* The use of the term accumulator plant for all plants that can be sampled for a given metal is misleading. Many plants used successfully by biogeochemists contain lesser concentrations of the metal sought than does the underlying soil. The plants sample the soil but they do not necessarily accumulate the metal.

aempt to establish a correlation in metal uptake
n them through sampling both plants together at
d locations. Usually, though, geological considera-
sor the distribution of already known deposits
t the size of the area to be sampled and a single
a e plant species can be found throughout.
h purpose of an investigation dictates, in most in-
s, the number of samples to be collected. If the
ion of a known ore body is the object of an in-
ation, perhaps then fewer samples will be required
ieve the objective than if a totally unknown area
ig investigated. In the former case the general
i of the ore body affords a starting place from
traverses can radiate. Moreover, if the deposit has
ir trend the problem is narrowed to sampling the
eyond the extremities. If the area is entirely un-
it is necessary to sample quite intensively. In
l a widely spaced grid pattern will give, at the
of a program, some indication of where the favor-
ocalities lie. After this preliminary attempt, de-
work in likely areas may establish the limits of a
t. Various means have been employed to collect
m samples such as the leaf punch, which cuts out
area of plant material, but this technique fails to
nto account the variable thickness of the leaf.
s, cutters and other garden devices have all been
ut none with any particular advantage. The type
ting tool to use is best left up to the individual and
the metal from which it is made contributes to the
nination of a sample, little concern need be given
hase of the operation.
ood deal of attention has to be given to the
rs of contamination. Plants can become contami-
in two important ways before they are sampled.
been demonstrated that wind blown material from
s and smelters poses a serious problem in some
and soil contamination through rain-spattering
nstant hazard when plants are sampled too close
surface of the ground. In areas where contamina-
likely, organs such as twigs should be sampled in
ence to leaves, because the ratio of total contami-
area to the volume of the organ is much less in
se of twigs than in the case of leaves. If there is
oubt as to whether a sample is contaminated or
t can be carefully washed in a dilute solution of
chloric acid. This procedure will be sufficient in
cases to remove contaminants. Some prospectors
ie bark from twigs to remove surficial dust. Others
wash the samples in distilled water with or with-
detergent. Lest this phase of the operation be
too lightly, it has been demonstrated that the
t of metal picked up by the hand from turning a
doorknob is sufficient to produce a positive metal
n with the reagent dithizone.
plant samples are taken to the laboratory in
paper bags where they are dried and ashed under
rd conditions. Since the metal content is usually
ated in terms of the ash weight (agronomists com-
use "dry weight") and since the weight of "ash"
ced from a given amount of dried plant depends
the length of time and the intensity of heating
specially important that this procedure be stand-
d. Ashing temperatures above 450° centigrade may
volatilization of some elements. The ash is weighed
and analysed for the metal sought by one of several techniques. Rapid, accurate wet chemical procedures have been developed for zinc, copper, "heavy metals," molybdenum, uranium, and nickel. Spectrographic analysis is sometimes used where the equipment is available. It provides a permanent record, has a high degree of sensitivity, and can analyze for several elements at once.

Contamination is a serious problem at this stage also. It has been suggested that the high concentration of lead and other metals in wall paints, for example, makes them important sources of error where uncovered samples are placed near old flaking paint.

The analyses, usually reported as parts per million (ppm) of metal in the plant ash, are plotted on a map and interpretations may then be made for areas of possible mineralization.

The technique is thought to have some advantages and some disadvantages as compared with analysis of soils directly for their metal content or with other prospecting techniques.

Advantages

(1) The metal content of several plants at each station is likely to be a more representative sample of the area than is the metal content of a few grams of soil. The plant roots themselves sample a large volume of soil.

(2) Sampling is rapid and easily done, and is therefore, inexpensive.

(3) Plant roots have access to large amounts of soil well below the surface. This can be an important factor because the concentration of the metal near the surface of a soil may tend to correlate with purely surficial conditions and be unrelated to the concentrations deeper in the soil. Moreover the migration of metals in soil can be extremely slow. Lundblad et al. (1949) have shown, for example, that of the copper supplied in large amount (250 Kgm per hectare) to the surface of a peaty copper deficient soil, only 2 percent had penetrated to a depth 5 centimeters below the soil surface 6 years after application. Most of the copper was fixed in the upper peaty layers. Nevertheless crops grown thereon did take up copper.

(4) If plants do accumulate metal concentrations greater than those present in the soil the analysis of plants may be simpler than direct analysis of the soil. Usually this is not a major factor.

Disadvantages

(1) The added step of ashing the plant for analysis is not required in soil analysis unless organic matter interferes with the analytical procedure.

(2) The unknown influences of many complex and many unknown factors in addition to metal content of the soil that affect the uptake and storage of metals by plants.

The more important known factors will be discussed below and an attempt will be made to estimate whether such factors are likely to produce variations in the metal content of plants so large that under some natural conditions they may obscure the variations in metal content in the soil. It should be pointed out, however, that soil analysis itself is not free of such complications. Surficial soil can be enriched in metal though the accumulation of plant debris, "Goldschmidt enrichment"; and is therefore subject also to the complications of plant metabolism. According to Mitchell (1955, p. 269-70), Goldschmidt enrichment appears to apply to Scottish moorland soils, on an ignition weight basis, for Ag, Cu, Mo, Pb, Sn, and Zn, but not for Co, Ni, Cr, V, Mn, Ti, Ga, Li, Rb, Ba or Sr. The effect is strongest where the metal enters into insoluble combinations with organic or inorganic materials. In addition the metal content of surficial soil may be in large part dependent upon the abundance of soil materials that are capable of selectively absorbing and binding or fixing metal ions. Micro-organisms in the soil commonly are major factors in controlling metal mobility in the soil. Inasmuch as direct soil analysis has become a standard adjunct to other exploration techniques in many places, and since the results obtained may depend in large part upon biological enrichment of the upper layers of the soil, it is desirable that geologists and others involved in this work

SAMPLER PLANTS FOR BIOGEOCHEMICAL PROSPECTING†

Plant name		Metal detected																				
Common	Scientific	Cu	Zn	Al	Se	Hg	Ge	Fe	Au	B	U	Mn	Ni	Mo	Ag	Sn	W	V	Sr	Co	Mg	Ba
Green alder	Alnus sinuata	x	x					x				x										
Willow	Salix sp.	x	x							x		x										
Scrub oak	Quercus tubinella	x																				
Emory oak	Quercus emoryi	x																				
Mountain mahogany	Cercocarpus ledifolius		x																			
Mountain hemlock	Tsuga mertensiana	x	x																			
Balsam fir	Abies amabilis	x	x																			
Giant cedar	Thuya plicata		x																			
Lodgepole pine	Pinus contorta	x	x					x	x	x		x			x							
Black cottonwood	Populus trichocarpa	x	x					x		x		x										
Larch	Larix occidentalis	x	x							x		x										
Aspen	Populus tremuloides	x	x					x	x	x		x			x							
Soolpolallie	Shepherdia canadensis		x							x		x										
Douglas fir	Pseudotsuga taxifolia	x	x					x	x			x			x							
Western red cedar	Thuja plicata	x	x					x				x										
Western hemlock	Tsuga heterophylla	x	x					x				x										
Rocky mountain juniper	Juniperus scopularum	x	x																			
Juniper	Juniperus sp.							x			x	x										
Pinyon pine	Pinus monophylla										x											
Ponderosa pine	Pinus ponderosa	x	x					x				x			x							
White bark pine	Pinus albicaulis	x	x																			
Englemann spruce	Picea engelmanni	x	x					x				x										
Sitka spruce	Picea sitchensis	x	x																			
White spruce	Picea glacua	x	x					x				x										
Dwarf juniper	Juniperus communis	x	x						x						x							
Rocky mountain fir	Abies lasiocarpa	x	x						x						x							
Scrub birch	Betula glandulosa	x	x																			
Mountain birch	Betula occidentalis	x	x																			
Silver birch	Betula popyrifera	x	x																			
Syringa orange	Philadelphus lewisii	x	x																			
Mountain maple	Acer glabrum	x	x					x				x										
Apple	----------		x																			
Poplar	Populus grandidintata		x																			
Western red birch	Betula fontinalis							x				x										
Grand fir	Abies grandis							x				x										
Willow	Salix scouleriana							x				x										
Red alder	Alnus rubra							x				x										
Broad leaf maple	Acer macrophyllum							x				x										
Vine maple	Acer circinatum							x				x										
Citrus	----------							x													x	
Choke cherry	Prunus demissa	x	x																			
Flowering dogwood	Cornus nuttallii							x				x										
Sumac	Rhus typhina		x																			
	Sassafras variifolium		x																			
Soft maple	Acer saccharinum		x																			
Pignut	Carya cordiformis		x																			
	Carya ovalis obvalis		x																			
Hickory	Carya ovata		x																			
Flowering dogwood	Cornus florida		x																			
Black walnut	Juglans nigra		x																			
Red cedar	Juniperus virginiana		x																			
Osage orange	Maclura pomifera		x																			
Sycamore	Platanus occidentalis		x																			
Black cherry	Prunus serotina		x																			
White oak	Quercus alba		x																			
Red oak	Quercus borealis maximus		x																			
Bur oak	Quercus macrocarpa		x																			
Blackjack oak	Quercus marilandica		x																			
	Quercus muhlenbergii		x																			
Pin oak	Quercus palustris		x																			
Post oak	Quercus stellata		x																			
Black oak	Quercus velutina		x																			
Sumac	Rhus copallina		x																			
Black locust	Robinia pseudoacacia		x																			
Nees	Sassafras albidum		x																			
Winged elm	Ulmus alata		x																			
American elm	Ulmus americana		x																			
Slippery elm	Ulmus fulva		x																			
Pine	----------																	x				
Hickory	----------							x				x									x	
Sugar maple	Acer saccharum																					
Princess pine	Lycopodium fabelliforme			x																		
Pecan	----------																					
Brazil nut	----------																					x
Chestnut	----------																					
Oak	Quercus wislizeni													x								x
	Pseudotsuga douglasii																					x
	Afzelia africana		x												x							
	Rubiacaea sp.		x												x							
	Bahia nitida		x												x							
	Parinari curatellifolia		x												x							
	Albizzia zygia		x												x							
	Lophira alata		x												x							
	Vitex cuneata		x												x							
	Parkia oliveri		x												x							
	Millettia sp.		x												x							
	Newbouldia lavis		x												x							
	Trichilia prievriana		x												x							
	Anacardiaceae sp.		x												x							
	Sp. indet		x												x							

SAMPLER PLANTS FOR BIOGEOCHEMICAL PROSPECTING—Continued

Plant name		Metal detected																								
Common	Scientific	Cu	Zn	Al	Se	Hg	Ge	Fe	Au	B	U	Mn	Ni	Mo	Ag	Sn	W	V	Sr	Co	Mg	Ba	Pb	RE
ak	Quercus douglasii													x										
ush	Artemisia tridentata							x				x												
	Gaultheria shallon							x				x												
uckleberry	Vaccinium parvifolium							x				x												
cinnick	Arctostaphylos uva-ursa							x				x												
box	Pachystima myrsinites							x				x												
	Corylus californica							x				x												
erry	Vaccinium sp.	x	x																					
s club	Echinopanax horridus	x	x																					
en	Pteridium aquilinum	x	x																					
spray	Holodiscus discolor	x	x																					
ite	Prosopis juliflora	x																						
etch	Astragalus sp.				x																			
ricegrass	Oryzopsis hymenoides				x																			
ale	Atriplex confertifolia				x																			
	Vaccinium vitis idaea	x	x										x											
	Ledum palustre	x	x										x											
ails	Equisetum sp.								x						x									
	Vaccinium ovalifolium	x	x																					
erry	Symphoricarpos racemosus	x	x																					
rush	Artemisia trifida	x	x																					
	Viola calaminaria*		x																					
	Thlaspi calaminaria*		x																					
	Amorphia canascens*																						x	
	Viola tricolor*		x																					
	Thlaspi alpestre*		x																					
	Asparagus officinalis		x																					
and eggs	Linaria vulgaris		x																					
over			x																					
	Zea mays		x																					
	Euphorbia maculata		x																					
n rod	Solidago sp.		x																					
ail	Equisetum arvense		x																					
	Lobelia inflata		x																					
	Lobelia syphillitica		x																					
in	Plantago lanciolata		x																					
	Pycnanthemum flexuosa		x																					
ed	Ambrosia artemisiifolia		x																					
ush	Amelanchier canadensis		x																					
n seal	Smilacina racemosa		x																					
	Tomanthera auriculata		x																					
	Viola sagittata		x																					
arrot	Daucus carota		x																					
v	Achillea millefolium		x																					
d cherry	Physalis sp.		x																					
erry	Celtis occidentalis		x																					
weed	Persicaria hydropiper		x																					
ed	Ambrosia coronopifolia		x																					
ed	Ambrosia elatior		x																					
ragweed	Ambrosia trifida		x																					
estem	Andropogon furcatus		x																					
bluestem	Andropogon scoparius		x																					
ne	Apocynum sibiricum		x																					
ed	Gnaphalium obtusifolium		x																					
wer	Helianthus mollis		x																					
	Liatrus aspera		x																					
	Desmodium sessilifolium		x																					
eed	Phytolacca decandra		x																					
	Salvia pitcheri		x																					
grass	Sorghastrum nutans		x																					
ush	Symphoricarpos orbiculatus		x																					
	Tridens flavis		x																					
ed	Vernonia interior		x																					
oon	Amelanchier alnifolia	x	x																					
																		x						
																		x						
																		x						
	Calluna rulgaris															x								
leaf				x																				
noss				x																				
w beauty				x																				
				x																				
				x																				
clover																				x				
clover										x														
	Polycarpia spirostyles	x																						
	Thymus serpyllum	x																						
	Viola hirto	x																						
o												x												
aster														x										
paint brush														x										
pea														x										
	Astragalus racemosus				x																			
	Oonopsis condensata				x																			
	Astragalus bisulcatus				x																			
	Xylorhiza parri				x																			
	Astragalus pectinatus				x																			
	Astragalus grayii				x																			
	Aplopappus fromantii				x																			

SAMPLER PLANTS FOR BIOGEOCHEMICAL PROSPECTING—Continued

Plant name		Metal detected																				
Common	Scientific	Cu	Zn	Al	Se	Hg	Ge	Fe	Au	B	U	Mn	Ni	Mo	Ag	Sn	W	V	Sr	Co	Mg	Ba
	Stanleya pinnata				x																	
	Gutierrezia sarothrae				x																	
Dandelion		x																				
	Arctostaphylos viscida																					x
	Adenostoma fasciculatum																					x
	Vivia americana													x								
	Medicagohispida													x								
	Lotus corniculatus													x								
	Trifolium repens													x								
	Trifolium fragiferum													x								
	Trifolium subterraneum													x								
	Melilotus alba													x								
	Melilotus indica													x								
	Melilotus sativa													x								
	Triticum vulgare													x								
	Avena sativa													x								
	Hordeum vulgare													x								
	Chloris gayana													x								
	Lolium perenne													x								
Rothrock gramma grass	Bautiloua rothrockii*	x																				
California poppy	Eschscholtzia mexicana*	x																				
	Holostium umbellatum					x																
	Viscaria alpina*	x																				
	Melandrium dioecum*	x																				
Carnation	Polycarpaie spirostylus*	x																				
Wild rose	Rosa woodsi*	x																				
Horsetail	Equisetum variegatum*	x							x													
Bush cinquefoil	Dasiphara fruticosa*	x																				
	Cneoridium dumosum													x								

† Compiled from various published and unpublished sources.

have some knowledge of the main factors influencing the uptake and storage of metals by plants.

Present Status of the Method

Elements that have been successfully detected by biogeochemical methods are: zinc, copper, lead, tin, tungsten, molybdenum, nickel, chromium, uranium, beryllium, manganese, gallium, strontium, silver, barium, mercury, cobalt, titanium, iron, and gold. A review of the agricultural data shows that aluminum, arsenic, silicon, selenium, germanium, boron, lithium, vanadium, iodine, magnesium, and the rare earths are known to accumulate in plants and therefore can be detected by biogeochemical means.

The accompanying table lists plants that have been successfully used in biogeochemical studies and others that, according to the agricultural data, probably could be used. The table includes both indicator and accumulator plants although the indicators represent only 8 percent of the total. Further, the table shows the dominant use of trees over all plants except that there are no indicators represented among the trees.

Previous Work. The areas in which biogeochemical studies have been conducted are many and diverse. The greatest activity has centered in North America, principally in Canada, with much of the work being done by the University of British Columbia and the Canadian mining industry. Pioneer work in the United States has been led by the U. S. Geological Survey. European contributions have come from Finland and Sweden. Russia has undoubtedly done considerable work in this field in an effort to develop her industrial potential.

The number of commercial organizations using geochemical prospecting in their exploration programs is unknown but apparently very large. Soil sampling and analysis is more popular than biogeochemistry and has become a standard prospecting technique for many private groups in Canada and in the United States. The U. S. Geological Survey, as well as several universities, is actively engaged in the development and imp[rove]ment of geochemical techniques.

The U. S. Geological Survey has developed quick [soil], water, and plant tests for various metals that ca[n be] performed in the field. Recently the Survey has us[ed a] portable grating spectrograph mounted on a two[-ton] truck. Geochemical programs have been carried ou[t in] at least ten major mining districts and in the dev[elop]ment of uranium exploration in the southwest. [Tests] have been developed for the detection of zinc, ni[ckel], uranium, and molybdenum in plants. These tests [are] designed to give plus or minus 30-50 percent accu[racy] at the minimum rate of 24 to 30 samples per man-[day]. Under favorable conditions this figure can be raise[d to] 60 or as many as 80 determinations per man-day. [The] Survey has also conducted basic research in plant [and] metal relationships in an effort to expand the us[e]ness of biogeochemistry.

The University of British Columbia, with the coop[era]tion of the Canadian mining industry, has perfe[cted] various analytical testing techniques using dithizon[e as] an indicator for heavy metals. Some 5,000 separate [a]nalyses have been run on plant samples to detect an[oma]lous concentrations of copper, zinc, lead, molybden[um], iron, manganese, silver, and gold.

On the Colorado Plateau trees growing in sedimen[tary] formations have yielded samples indicating that ura[nium] may be concentrated at a depth as great as 60 feet ([Gran]non, 1953); the results of Canadian studies [show] mineralization can be detected through 50 feet of gl[acial] drift or 60 feet of muskeg swamp (Webb, 1953, p. 3[).]

The successful applications of biogeochemical p[ros]pecting fall into two groups: studies over known [ore] bodies and the actual location of new ore deposits [by] the former case the record is marked by varying deg[rees] of success. The work of Webb and Millman, Vogt, [Har]baugh and others in some cases has shown a less [than] clear cut support of biogeochemical principles. [While] on the other hand Warren and Delavault, Sokol[off,]

i', Hawks, Raukama and many more have achieved
icant success in their investigations. The great ma-
t of evidence cited in the literature supports the
ses on which biogeochemical prospecting is based,
h undoubtedly there have been a great many un-
sful attempts not reported in the literature.
ical examples of successful applications over
ı ore deposits are found in the work of Warren
lawatson (1947) on copper and zinc mineralization
nada. Studies were made in several copper camps
extensive mining operations had definitely out-
positive and negative areas. Tree samples were
sed and the results between positive and negative
were compared. In one area five different tree types
owed marked variation in copper concentration
en the mineralized and nonmineralized areas; one
s differed nearly a hundred fold in concentration
the smallest variation was threefold. The average
r concentration for all five trees in the positive
was 13,080 ppm copper as opposed to 560 ppm
r in the negative area.
geochemistry has played an essential role in lo-
small bodies of uranium (Cannon, 1953), vana-
(Cannon, 1953), and iron, and chromium (Buck,
. This method has also been successful in locating
d, pinched, and otherwise hidden extensions of
n ore bodies. A number of near-commercial de-
, such as the chalcopyrite mineralization in the
roo mining district of South Australia, have been
(Harbaugh and Starrett, p. 32, 1953; Webb, p.
1953). Cannon and Starrett (1956) have combined
se of plants as indicators and as samplers for
um.
ile the discoveries of new ore are not as spectacular
ne might expect from the success of empirical
es, it has been stated that they more than paid for
ntire cost of all exploratory and experimental work
within the last several years (Webb, p. 344, 1953).
the other hand the results from biogeochemical
ecting have not been uniformly reliable. Anoma-
variations in the metal content of plants have been
which are so haphazard in their distribution that
could not be used safely to plan more expensive
rface exploration. The uptake of some minor ele-
s is not necessarily proportional to their relative
nts in the soils.

ABSORPTION OF METALS BY PLANTS

ants obtain mineral salts from the soil by (1) ion
lt accumulation, (2) ionic exchange, (3) chemical
ination, and (4) by diffusion. The absorption
ess is highly selective, some cations, anions and
cules being effectively accumulated while others are
ded to a remarkable degree. Ion accumulation is
process by which ions may accumulate in much
er concentrations within the plant cells than the
entration of the same ion in the medium surround-
he plant. This is an energy-expending process tak-
place largely in young growing cells especially near
tips and continuing only while oxygen supply and
erature are conducive to aerobic respiration in the
t. Since aerobic respiration is dependent in turn
the supply of carbohydrates and other organic
rials produced by photosynthesis in the upper or-
gans of the plant, the rate of ion accumulation tends to fall with any conditions that reduce markedly the rate of photosynthesis. Ion accumulation may tend to vary also with the rate of transpiration by the plant and in addition, ions of one species may have an effect upon the uptake of ions of other species.

Ionic exchange mechanisms permit the exchange of anions or cations from the root surfaces of the plant for anions or cations in the soil. Ionic exchange is probably not a metabolic process, does not require expenditure of energy by the plant and occurs independently of aeration or temperature. Carbonic acid or possibly organic acids produced by the roots and absorbed on the root surfaces releases hydrogen ions which then may be exchanged for other cations in the soil fluid or those sorbed on soil materials. Entry of ions by combination is similar to their entry by ion exchange. In this process, however, the ion may become a part of a metal-organic complex. Iron and magnesium are so absorbed; copper, zinc, manganese, molybdenum, cobalt and aluminum may enter such compounds, though knowledge of this process is very limited.

Simple diffusion from soil to plant is not now thought to be an important primary process for mineral salt assimilation though it may contribute in some favorable circumstances. Nor do mineral nutrients merely travel along with the water absorbed. Diffusion plays an important role in the soil quite outside the plant and assists in the translocation of ions once they have entered the plant.

Thus the amount of metal taken up from the soil by a plant is influenced by factors that control the health and metabolism of the plant and also by many factors that control the availability of metal ions to the plant. If these factors vary markedly along a sample traverse in a biogeochemical survey, or if they vary throughout the area sampled, the analyses of the plant samples will reflect these factors as well as, or perhaps to the exclusion of, variations in metal content of the soil. Presumably, then, these factors might produce misleading anomalies in plant metal content, suggesting a concentration of metal in the soil that does not exist. Or they may mask a real concentration of metal in the soil above a metal deposit. On the other hand, the effect of some of them may be slight in comparison with the variation observed in plants from ore-bearing to barren areas. In any event prospectors attempting to use the biogeochemical method should be aware of these factors and should have a rough idea of their possible influence on survey results. Unfortunately the subject is complicated and the data for many metals of interest to prospectors is meager. Nevertheless some suggestions might be obtained as to the approximate size of the variation in plant metal content that is needed to justify additional expenditures for detailed exploration.

It will be obvious in the following that the authors, who are geologists, are heavily indebted to agriculturalists and plant physiologists as well as biogeochemists for the data summarized.

Factors Related to the Plant

Kind of Plant. Warren and Delavault have concluded, after considering the results obtained from hundreds of plant analyses, that practically all trees and

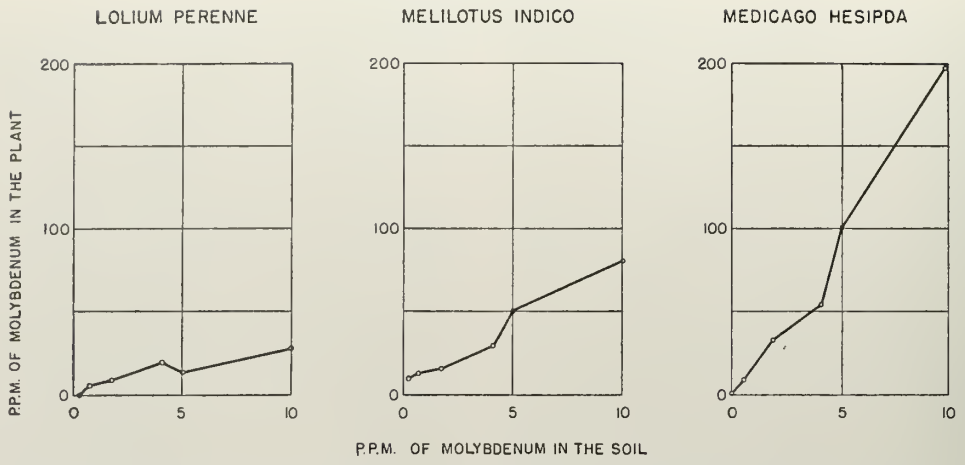


FIGURE 2. Graphs showing how different types of plants, growing under the same conditions, will take up different amounts of molybdenum from the soil. *Data from Barshad (1951).*

smaller plants are capable of reflecting mineralization. Any number of plant types can be used in sampling a given area but each will give a different biogeochemical anomaly which may vary considerably. While the pattern of the anomaly will generally be preserved, there is a chance that an anomaly could be overlooked if the plant type sampled absorbs only minor amounts of a given metal. The relative absorption of molybdenum by three different plant types serves to illustrate this problem. If at the beginning of a prospecting program one chose to sample *Melilotus indica* and during the course of a traverse changed to *Medicago hespida* the molybdenum content would increase by as much as 125 parts per million. This increase could be interpreted to mean the existence of an underlying ore-body whereas the metal content of the soil actually had remained constant. If on the other hand *Lolium perenne* were sampled at the same point a drop of 40 parts per million would be expected, and one might conclude that a mineralized area lay behind. Yet the plant type would be the only factor responsible for the variation.

Table 1. Nutrient Requirements of Different Plants.

Plant	Element (%)		
	Ca	K	Mg
Sunflower	2.18	5.01	.640
Beans	2.11	4.02	.594
Wheat	.79	6.73	.406
Barley	1.87	6.92	.540
Peas	1.55	5.25	.504
Corn	.51	3.87	.402

After Newton (1928)

An even more striking example is the accumulation of selenium by certain species of *Astragalus*. In one investigation (Trelease, 1945), the average content of these accumulators was about 800 ppm, some plants containing as much as 15,000 ppm (1½ percent), many times the amount that would be lethal to ordinary plants. Wheat from the same soil averaged less than 5 ppm of selenium.

Large differences may exist between families, species, or varieties in their ability to absorb a given element under a given set of conditions. Many plants require abnormal amounts of molybdenum; horsetails absorb silica; and members of the family *Lycopodioceae* accumulate aluminum. Even the normal uptake of major ents varies within wide limits among plants of di groups. Table 1, modified from Newton (1928) illus the varying requirements of calcium, potassium magnesium by six common plants. All six plants grown in nutrient solution for 56 days, with five individuals of each type in the same crock. On green portion of each plant was analyzed.

The data of Collander (1941) showing variati uptake between plants are even more striking. The mum uptake for Na and Mn is about 20 to 60 greater than the minimum; for Li, Mg, Ca, an about 3 to 5 times the minimum; for K, Rb, an about 2 to 3 times the minimum. A given plan found to be consistently rich or poor in a given el regardless of the year of cultivation or the compo of the culture solution. An interesting relationship by Collander and also by Hurd-Karrer (1939) great similarity in the uptake by a given plant c ments that are chemically alike. Rubidium and c were found to be absorbed almost as rapidly as sium; strontium almost as rapidly as calcium; sele as fast as sulfur, and arsenic as fast as phosph Some plants appear to be able to screen out or to themselves against excessive uptake of some elen Plants do not contain silicon and aluminum, for ple, in proportion to their abundance in the soil. M algae generally contain abundant potassium and little sodium, although the concentration of thes ments in sea water is in the reverse ratio. Pea roots found to absorb 2 to 3 times as much calcium Na-Ca bentonite as did barley roots, while at the time barley roots absorbed 4 to 5 times as muc dium as did pea roots (Elgabaly and Wiklander, 1 This is an effect that varies markedly between types, is different for different groups of elements soil materials and is likely to become known only extensive experimental work. Unfortunately almost ing is known about selective uptake of the micronutr or of metals present in minor amounts. In the ca sodium and calcium just described the disproportio uptake is reduced when the concentration of sodium calcium outside the plant is increased.

le roots of rice were found to protect themselves
further absorption of copper ions after they had
bed a certain amount (Isizuka, 1940). In another
Melandrium silvestre plants that had already grown
pper-rich soils were found to grow better than
s under experimental conditions of high copper
ly and in still another case large increases in the
nt of zinc in the soil did not result in proportionate
ases in the zinc content of the oat plant.

e are not aware of any cases, however, where selec-
uptake or shielding by healthy plants has been
n to result in a reverse relationship between metal
nt of a plant and metal content of the soil in which
plant is growing, all other conditions remaining
ant, although there are cases where the variation
ant metal content is negligible.

e experience of biogeochemical prospectors indicates
trees in general are more consistent in reflecting
netal concentration of the soil than are smaller
s. But the lesser plants in many instances show a
er contrast in metal concentration than do the trees
ing in a given area. The giant ragweed *Ambrosia*
a sampled by Harbaugh (1950, pp. 564-565) in the
tate district showed a variation in zinc content
5000 ppm to 1500 ppm between the mineralized
and the barren area. Among the trees the black
y (*Prunus serotina*) showed the largest variation;
nged from 2200 ppm zinc in the mineralized area to
ppm zinc in the barren area. Webb and Millman
l, p. 495) noted in their biogeochemical studies in
a, that there was little variation in metal content
en species. They showed that the background
s were especially constant among different plants
buted over wide areas.

nt Organ Sampled. After the absorption of soil
rials by the roots, each element travels to specific
of the plant structure. The translocation, or route
destination, of these nutrients is important in choos-
which organ to sample. In general, the newly ab-
d materials travel to the younger parts of the
. Therefore, these parts contain the highest concen-
n of metal and are the most satisfactory to sample.
ever, Warren and Delavault (1949, p. 541) working
copper and zinc in British Columbia, found that
eaves, cones, and needles of trees gave inconsistent
ts. They recommend the use of twigs which were
1 to 3 years old and an eighth to a quarter of an
in diameter. The data summarized in table 2 are
on nine biogeochemical investigations which in-
d 75 tree samples, 13 samples of smaller plants, and
iety of metals. The organs are arranged in order of
asing metal concentration. In the tree samples the
s showed the highest concentration of metal in 49
nt of the analyses, and the twigs were highest in
ercent of the samples. The leaves contained the
st concentration in 77 percent of the smaller plants.
toradiographs taken by Biddulph and reported by
g (1951, pp. 261-275) substantiate the results tabu-
above. Biddulph introduced radioactive phosphorus
a nutrient solution which contained young bean
s; half of these were sampled after a period of four
and the others were transferred to fresh nutrient

Table 2. Organs with the highest metal concentration (in order of decreasing concentration).

Trees	Smaller plants
1. Leaves	1. Leaves
2. Twigs	2. Roots
3. Cones	3. Stems
4. Wood	
5. Roots	
6. Bark	

solution which contained no phosphorus. The plants sampled after the first four days showed that the phosphorus had moved directly through the roots to the younger portion of the plants. The remaining plants were sampled after an additional four days and autoradiographs were made of them. The second set of graphs showed that a considerable amount of the phosphorus deposited in the younger organs, at the time of transplanting, had moved to the new plant organs developed during the second four-day period. Thus, not only is there a continuous influx of material from the roots to the younger organs but there is also a constant redistribution of material to the younger leaves and twigs.

Age of Plant and of Plant Organ. After a plant reaches a certain minimum age, which is different for each plant type, the uptake of material from the soil—all other things being equal—becomes constant and the requirements of new growth cause only gradual increases. While the plant as a whole may show no sharp variation in nutrient content, the individual organs developed during different growing seasons exhibit marked variations. Table 3, from Barshad's work with molybdenum, contrasts the metal content of new tree leaves with those of the previous year's growth. Tree organs from 1 to 3 years old give consistent results in addition to containing the maximum concentration of metal. Younger organs fluctuate in metal content while the oldest wood consistently shows low concentrations.

The smaller plants reach a similar optimum at the time of flowering when the metal concentration is at a peak and the leaf functions are fully developed (Lundegarth, 1951). For these reasons the whole of a traverse or area should be sampled at about the same time.

The combined effect of sunlight, rainfall, air temperature, as well as the plant itself is responsible for the seasonal variation of metal uptake by plants. Robinson (1943, p. 6) has checked the same trees for rare earths on three different occasions. It was found on June 1 that the trees contained 174 ppm rare earths, on July 4 the total ppm had risen to 634, and by October 1, to 981 ppm. The same worker reported boron in samples of hickory leaves doubled between spring and fall (Robinson et al., 1942). Barshad shows molybdenum in certain plants varies three-fold from spring to fall. Warren et al. (1947, p. 806) have noticed the seasonal variation of copper and zinc in tree leaves.

Health of the Plant. If plant roots are injured through toxic soil conditions or in other ways they may lose their ability to absorb elements selectively or they may absorb excessive quantities of some elements. A single plant thus injured might yield an exeessively high assay which would not be duplicated in neighboring plants and should therefore be rejected. But if all the

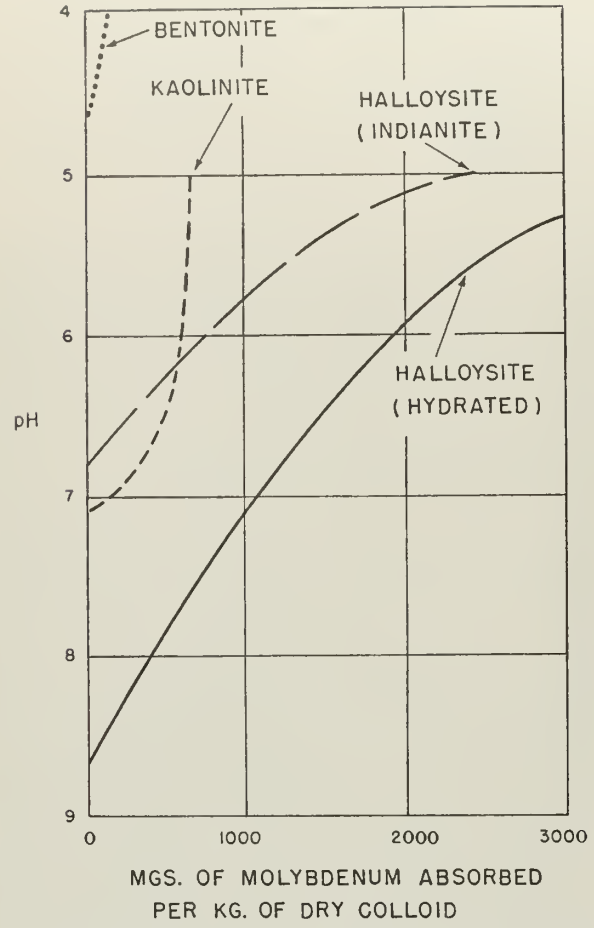


FIGURE 3. Graph showing amount of molybdenum absorbed by four types of clay minerals at different pH. *Modified from Barshad (1951).*

Table 3. Molybdenum content of new and old tree leaves.

Plant	Molybdenum in leaves (mgm./kgm.)	
	Current growth	Previous year's growth
Lemon tree	1.3	2.3
Mesquite	1.2	3.6

Modified after Barshad (1951)

plants within one segment of the area under survey are injured in the same way, this segment would yield high assays and unless the condition of the plants was recognized from some fairly obvious abnormality the anomalous segment might be treated as a valid suggestion of mineralization. Biogeochemical anomalies that correspond with marked differences in the physical character of the soil should be suspect.

Root Depth. The maximum depth at which a biogeochemical anomaly can be detected at the surface is determined principally by two factors: the depth to which the plant roots extend downward and the ion-dispersing forces working from the ore body upward.

The root systems of most plants extend into the soil only a few inches or feet at the most. While some root systems extend to depths of 80 feet and more, in gen deep roots are exceptional. Weaver (1919) limits root depth of herbs and shrubs growing on the f floor to the upper 18 inches. Kelley (1923, p. 15) re that the absorbing system of most woodland plan concentrated within the soil's upper 12 cm and depth of 30-70 cm. Further, he questions the ge assumption that trees have deeply penetrating tap r

The root depth appears to be less important in s ing out high metal concentrations in the soil than the forces that raise the ions from depth. Many bio chemical studies have utilized both trees and l plants in a single investigation (Warren and Howat 1947). There was no evidence to suggest that trees able to tap high metal concentration at depths reached by shallow-rooted plants.

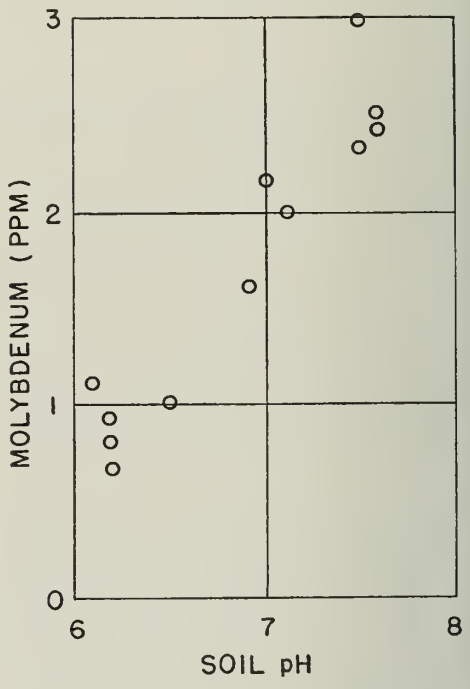


FIGURE 4. Graph showing amount of molybdenum taken up by alfalfa at different pH. Assimilation increases with decreasing soil acidity. *Data from Evans, Purvis, and Bear (1951).*

Chemical and Physical State of the Metal

Metals in the Soil Solution and in Mineral Gr The soil is the principal source of the macronutri water, phosphorus, sulfur, potassium, calcium, ma sium and iron; the micronutrients, copper, zinc, mo denum, manganese, boron, and possibly silicon, co and others, as well as the many metals not yet sh to be of nutrient value to plants.

Metals may simply be dissolved in soil water and s readily available to plants. There is also abundant dence that plants can take metals directly from s minerals. A slowly soluble form of copper, for insta is commonly adequate for plant growth (Jamison, 19 The form in which zinc is available—as zinc carbon freshly applied zinc sulfate, zinc applied in plant

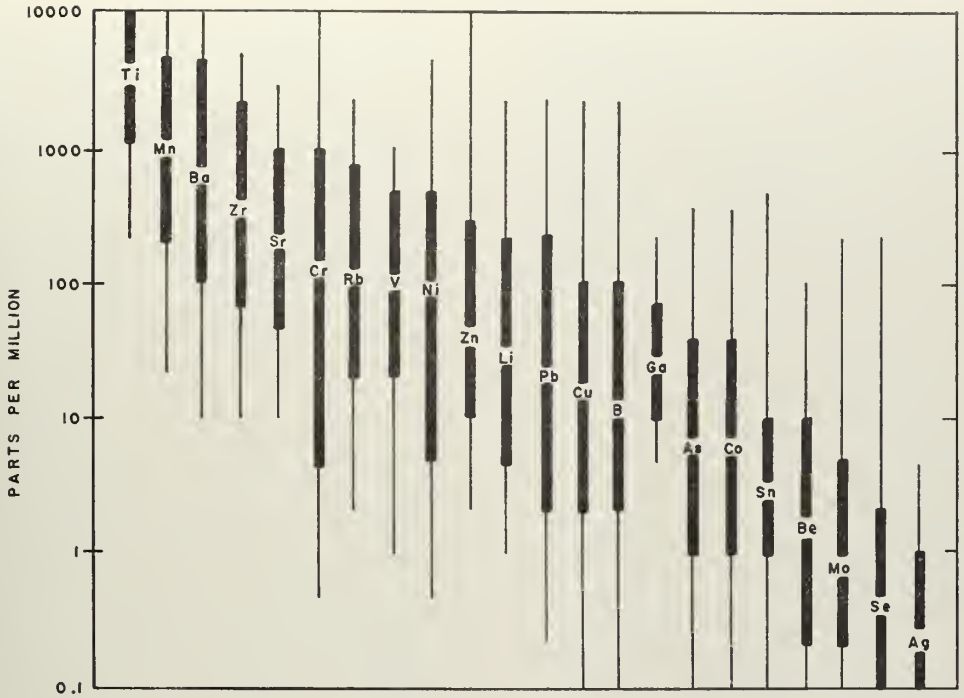


FIGURE 5. "Range of contents of some trace elements commonly found in mineral soils. Thin lines indicate more unusual values; certain extremely high contents reported from abnormal localities influenced, for instance, by ore deposits have been ignored." *From R. L. Mitchell, in Chemistry of the Soil, F. E. Bear, Editor, 1955. Courtesy Reinhold Publishing Corporation.*

ıl, or zinc accumulated in the soil from applications nc sulfate over 5 years—makes very little difference ts utilization by a plant (Shaw, Menzel and Dean, ł). Plants are able to obtain phosphorus directly ı relatively insoluble soil- or rock-phosphate, al- gh the ability to do so varies greatly from plant lant. Manganese may be available from very fine- ned manganese oxides (Jones and Leeper, 1951).

etals Held in the Soil by Ion Exchange. In typical of temperate regions, only a small fraction of the l metal content available to plants is present as dis- ed ions in the soil water or as a major component of eral grains. The larger part is sorbed [1] as cations or nions on various colloidal particles, principally clay erals and organic matter; it is bound to them with ds of varying strength and is therefore differentially lable to plants. Were it not sorbed in this way, most he mineral matter added to soils as soluble salts— n fertilizers, for example—would be leached rapidly n the soil and serve very little purpose. Or some me- c ions, only traces of which are required by the plant, ht be available in excessive, perhaps toxic, amounts. ome of the ions sorbed on colloidal materials are so tly bound that they are said to be fixed, and are ctically unavailable to plants under normal condi- s. Others can be released to the soil solution, or to nts directly, or perhaps to other soil colloids, by the stitution of suitable ions. As an example, all or nearly he potassium sorbed on a clay might be replaced by rogen and carried away in solution if the clay were leached with an acid. And subsequently the hydrogen might be replaced by potassium or by some other ion or ions through leaching again with a solution containing these ions.

This process whereby cations or anions are exchanged between liquids and solids, or between solid and solid, is ion exchange. It affects both organic and inorganic components, and influences both physical and chemical properties of the soil. An essential step in assimilation of mineral elements by plants is the direct exchange of hydrogen ions released by the plant for mineral ions in the soil. Apparently this can take place with or without intermediate solution of the ions. The ion-exchange process is like other ordinary chemical processes in many ways, being reversible, stoichiometric (retaining electrical balance) and dependent upon the concentrations of the exchanged ions. The rate of reaction ranges from instantaneous to several hours, depending mainly upon the exchange material on which the ions are sorbed. The predominant exchange materials in soils are clay and organic matter, though other very fine-grained substances possess exchange properties as well. Calcium carbonate, for example, is a very effective absorbing material in calcareous soils.

The cation exchange properties of clays are due to (1) Unsatisfied chemical bonds of clay crystal fragments balanced charges that can sorb cations (important in kaolinite and halloysite; less important in illite and chorite; and of minor importance in montmorillonite and vermiculite); (2) Unbalanced charges due to substitution within the lattice structure that may likewise be satisfied by sorbed cations (particularly in montmoril-

[1] ludes any process by which ions are held.

lonite and vermiculite); and (3) Cation replacement of the hydrogen in exposed hydroxyl ions (important in kaolinite and halloysite). Partly because there are these several causes of cation exchange and partly because the position of exchangeable cations relative to the clay mineral surface varies greatly, cations even of a given element are held with varying tenacity on a given clay mineral. Generally they are held with decreasing tenacity as the clay mineral becomes saturated with exchanged cations. Usually ions held as a result of broken bonds are around the edges of the clay crystals and are much more easily displaced than those held as a result of substitutions within the lattice structure. The relative energies with which cations of different elements are held, or the relative difficulty of displacing them, is not easily predicted. An order or replaceability Cu>Pb>Ni>Co>Zn >Ba>Ca has been suggested (Mitchell, 1955 p. 265); but in view of the several causes of ion exchange, probably no one order of replaceability applies for all exchange materials. Generally, but not universally, the difficulty of displacing a cation appears to increase with valence and with size of the ion, and tends to decrease with hydration of the ion. Reducing the size of the clay particles, as in grinding, tends to increase the capacity of the clay to exchange cations—especially clays in which the main cause of cation exchange is broken bonds.

The cation-exchange capacities of clay minerals, measured in milligram equivalents (m.e.) of cation held per hundred grams of exchange material at pH 7, ranges from 3 to 15 for kaolinite, from 5 to 50 for halloysite, from 80 to 150 for montmorillonite and vermiculite, and from 10 to 40 for illite, chlorite, and attapulgite groups (Grim, 1953, p. 129). Natural soils are reported with a cation-exchange capacity of 200 m.e. or more per 100 grams of soil. Peaty soils are reported to have the highest capacities. Inorganic soils rarely have exchange capacities exceeding 75 m.e., and the great majority have less than 50 m.e. per 100 grams of soil. A soil with an exchange capacity of 50 m.e. per 100 grams could absorb over 15,000 ppm of zinc. Other ions, if also present, would, of course, compete with the zinc for exchange positions. Exchange capacity increases with pH; that is, exchange capacity is higher under alkaline conditions. Generally the number of ions held tends to vary with its concentration outside the exchange material.

In addition to, or instead of being absorbed as cations, some metals such as boron, molybdenum, selenium, and vanadium can appear as complex anions which are soluble in water and can be absorbed as anions by anion-exchange materials. Others such as zinc, copper, ferric iron, and thorium may form basic salts with clay as well as being absorbed as cations (Mitchell, 1955, p. 264). And in general, the higher the percentage of saturation by a given cation, the more easily that cation can be displaced and absorbed by plants (Jenny and Ayers, 1939). Thus, in a kaolinitic soil with an exchange capacity of 8 m.e. per 100 g, of which 0.08 m.e. (1 percent) was copper, the amount of copper available to plants should be greater than in a montmorillonitic soil with a cation-exchange capacity of 40 m.e. per 100 g, of which 0.2 m.e. (0.5 percent) was copper. In general, the heavy metals are less readily available to plants from montmorillontic clays than from kaolinitic clays. The situation is complex where several ions compete fo change positions, the degree of saturation having tively little effect on availability where the other s ions are held very tightly but having a very large on availability where the other ions are held loose common result of this is that the availability of a l metal decreases as the ratio of sorbed sodium to s calcium increases.

Metals Held in the Soil Other Than by Ion Exch Through a process called "chelation" some metal able to form stable complex ions with certain or substances produced in soils. The metal thus che does not enter into reactions of its own but is ca along with the complex ion. It may be either less able or more available to plants than it was b chelation. Relatively insoluble compounds of co zinc, iron, manganese, aluminum and calcium ca converted to soluble forms through chelation. The appearance of zinc and manganese deficiency symp in plants under conditions favoring greater mic ganic activity, or when organic matter especially plant roots is added to the soil has been ascribed t formation of organic chelating compounds which the needed metals available (Mehlich and Drake, p. 322). Iron versenate and ferric citrate are che forms of iron that provide an available source of for plants. On the other hand, Crooke (1954) has s that nickel supplied as nickel versenate to oats in culture did not increase the nickel content of the p over that of control plants whereas nickel supplie the same amounts as the soluble ion from nickel su increased the nickel content in the plants more 10 fold, producing toxic effects. Therefore, the nick the nickel-toxic soil studied by Crooke he thought the chelate form associated with the soil organic m and thus was readily available to plants.

Under some conditions metals present as soluble may form relatively insoluble precipitates with si anions such as hydroxide, carbonate, phosphate or cate. That zinc, manganese, copper and cobalt ar creasingly available as the alkalinity increases result from this. Bivalent iron and manganese ca made much less soluble through oxidation to oxid hydrous oxides.

Fixation. The term fixation does not appear to a precise meaning. It is used by some people to ind merely retention of a metal in the soil in a form resists leaching by meteoric water and by others to cate greatly reduced availability to plants. Be metals can be held in the soil in so many ways ar such varying degrees there is no sharp distinctio tween those that are exchangeable or otherwise avai and those that are not. If the energy of binding particular cation to a clay mineral, for example, ex the cation exchange energy of a plant root, the c is unavailable to the plant. But other cations of the element sorbed in a different way may be avail Some of the zinc ions sorbed in some magnesium are thought to become incorporated within the cr lattice of the clay mineral and are not exchang (Elgabaly, 1950). The amount of nonexchangeable on kaolinite was found to increase with grinding o

lattice structure to destruction. Appreciable fixation tassium on montmorillonite occurs on drying and action of the lattice.

Chemical Properties of the Soil

The chemical composition of the soil, more than any- else, determines the chemical and physical state dence the availability of metals to plants. It also lences the amount of metal taken up by plants. co-organisms may compete for some nutrient metals, ny produce substances that make metals either more ls soluble in soil water. Of the several chemical var- l, the abundance of competitive or complementary und the pH of the soil can have marked effects on etal content of plants.

Acidity or alkalinity of a soil is probably the most rtant single factor likely to produce misleading re- in biogeochemical prospecting. It has some effect e vigor of plants and determines the distribution of plant types that are sensitive to a particular in pH. Most plants that have been studied by riculturists, however, tolerate a wide range of pH for wth if the necessary nutrients are available. Probably has its greatest effect on plant growth though con- ng the chemical state and availability of nutrient bances. It may completely immobilize a metal in the by causing its precipitation as an insoluble com- d. For example, carbonates and phosphates of cal- m and magnesium and carbonates, oxides and hy- xides of iron, copper, manganese, and zinc tend to n under alkaline conditions. Soil pH affects the ion nge properties of clays and other exchange ma- ls. In soils with pH varying in depth, the part of oot system that absorbs nutrients is governed by variation.

The normal range of pH in soils is between 3 and 9, ugh locally the pH may be beyond this range. Cer- plants thrive on abnormally acid or alkaline soils, he salt bush (*Atriplex*) and glasswort (*Silicornia*) ich prefer strongly alkaline soils. In general, plants best suited to neutral or slightly acid soils. The soil not constant and tends to become more alkaline depth. Kelley, working in Chester County, Pennsyl- nia reports the soil increases in acidity to a depth of centimeters then decreases (1948, p. 53). More com- te data by Barshad is summarized in table 4 (1948, 19).

Table 4. Examples of the relation of pH to depth in various soils. (After Barshad)

Depth range (inches)	pH range
0 to 80	7.3 to 7.5
0 to 60	7.3 to 9.1
0 to 36	7.6 to 8.1
0 to 48	7.5 to 6.8
0 to 60	7.3 to 8.1
0 to 36	8.4 to 9.7
0 to 48	7.9 to 9.3
0 to 72	7.9 to 9.4
0 to 30	6.4 to 6.7
0 to 56	5.6 to 5.5
0 to 43	5.6 to 5.2

Plants themselves acidify soils by exchanging hydro- ns at the root surface for soil nutrients. Parent ck tends to influence soil pH especially of residual ls where rainfall is low. Carbonate rocks, for example, tend to yield alkaline soils. But in areas of high rainfall the increased vegetation, the resulting humus and the leaching of more soluble alkaline components tends to produce acid soils. The mineral belts in California are, in general, in mountainous regions where the soils tend to be acid. Weathering of sulfide ore deposits tends also to acidify soils. Acidic surface waters are fairly common near ore deposits.

There is evidence to suggest that copper is fixed in alkaline soils. Experiments of Peech reported by Jamison (1942, p. 296) show that only 17 percent of copper added to soil remains available at pH 4.0 and only a trace at pH 6.0. A similar test by the same worker showed 40 percent recovery at pH 3.1 and 10 percent at pH 5.0 (1942, p. 295). However, Jamison reports somewhat different results, with a soil pH of 4.0 he recovered all of the copper and at pH of 6.0 only 33 percent (1942, p. 296). In spite of the lack of agreement in these data, it has been established that copper precipitation begins at near neutral pH and is complete in the alkaline range. Warren et al. (1952, p. 483), in field prospecting for copper, noted a similar influence of pH on the solubility of this metal.

The influence of pH on the solubility of zinc is much the same as on copper. Zinc is concentrated in plants growing in soils with a pH range of 3.5 to 7, with the majority of the samples having a pH of 4 to 5 (Fulton, 1950, p. 667). Robinson et al. (1947, p. 577) report that nut and fruit trees resist the absorption of zinc in alkaline soils. The solubility of zinc in alkaline soils can be materially increased by the addition of acid to the soil (Aldrich and Turrell, 1951, p. 89).

Manganese, like the previous two metals, is absorbed more readily by plants in an acid environment. Mulder and Gerretsen (1952, p. 229) have shown that manganese is highly soluble below pH 5.5 but with increasing pH the metal is converted to the manganic oxides (Mn^{+++} and Mn^{++++}) and as a result becomes less available to the plant. Brenchley et al. (1936, p. 182) have observed a similar reaction where manganese is unavailable to plants in alkaline soils. The same conclusion was reached by Fujimoto (1948, p. 132) working in Hawaiian soils and also by Aldrich and Turrell (1951, p. 89). Aluminum is reported to be available to plants in two pH ranges: 4.5 and below, and 8.0 and above (Mehlich, 1942, p. 121). However, previous work showed aluminum as the silicate is precipitated between pH 3 and 5 and also at pH 9 to 14 (Hartsock and Pierce, 1952).

Both tungsten and molybdenum are available in the alkaline pH range. Tungsten and molybdenum are precipitated as ochers in a pH range of 3 to 5 (Hartsock and Pierce, 1952; Clark, 1924). Molybdenum is extremely sensitive to slight pH changes in certain ranges. Barshad has shown that a pH change of 0.8 in an acid sandy loam resulted in a hundred percent increase of available molybdenum, and a pH change of 2.7 in a clay soil more than doubled the available molybdenum (1948, p. 189).

Other metals such as barium and boron have been studied by various workers. Roberts (1948, p. 74) reports that he found no correlation between barium content and pH. However, Mehlich (1942, pp. 121-122) reports the absorption of barium in inorganic soils

reaches a maximum between pH 8 and 9; in organic soils between pH 6 and 8. Brenchley (1936, p. 175) states that boron is unavailable to plants in the alkaline range (1936, p. 175).

The accompanying table summarizes the effect of soil pH on the availability of certain elements to plants.

Table 5. Effect of pH on the Availability of Elements to Plants

Elements more available in acid soils	Elements more available in alkaline soils
Aluminum *	Aluminum
Iron	Calcium
Manganese	Magnesium
Copper	Sodium
Zinc	Potassium
Boron	Molybdenum
Phosphorus †	Tungsten
	Selenium
	Silicon
	Barium

* Aluminum is available to plants in two pH ranges, (1) 8.0 and above, (2) 4.5 and below.
† Most available in mildly acid soils pH 6-7. Increasingly unavailable at pH < 5.0.

The uptake of a metal also can be influenced very strongly by other elements or radicals for reasons ranging from simple competition for exchange positions to very complex metabolic relationships that are not well understood.

For example, addition of phosphate in amounts likely to be used in ordinary fertilization practice has been found to cause the increase of the molybdenum content of crop plants as much as 10 fold. Addition of sulfate as gypsum decreased the molybdenum content of the plants as much as 6 fold (Stout, et al., 1951). Barshad (1951, II, p. 397) found the effect of phosphorous on molybdenum to be much more pronounced in acid than alkaline soils. Manganese sulfate inhibits the uptake of molybdenum by cauliflower and lettuce but not by spinach, tomato or white clover (Mulder, 1954).

The zinc content of oats decreased two- to four-fold with a 20-fold increase in the amount of calcium carbonate in the soil and decreased almost two-fold with a 15-fold increase in phosphate (Rogers and Chih-Hwa Wu, 1948). Zinc combining with phosphoric acid in the soil forms $ZnPO_4$ which is unavailable to plants (Robinson, et al., 1947, p. 597; Davis, 1941, p. 84). Increased soil nitrogen and potassium decreased the zinc content of orange leaves by as much as 5 percent (Reuther and Smith, 1950). Variations of two- or three-fold in the distribution of manganese in potato plants and in the manganese content were caused by altering the amounts of iron, potassium, phosphate, or calcium carbonate in the soil (Bolle Jones, 1955). Manganese tends to be available in the presence of sulfur, chlorides and iodides, but is fixed by fluorides and bromides (Fujimoto and Sherman, 1948). A significant increase in the uptake of nickel by oats was caused by an increase in the rate of supply of phosphorous but not by an increase in other major nutrients (Crooke and Inkson, 1955). Copper sulfate added to peaty soils decreased uptake of iron enough to cause chlorosis of corn plants (Willis and Piland, 1936). Similar interaction between iron and manganese, copper and nickel, copper and zinc, copper and molybdenum, copper and manganese, manganese and aluminum and calcium and manganese are also reported (Mehlich and Drake, 1955). The presence of such ions as Ca^{++}, Ba^{++}, Al^{+++} and Fe^{+++} has been observed to stimulat uptake of K^+, Rb^+, Cs^+ and Br^- under some cond (Overstreet and Jacobson, 1952, p. 190).

Certain elements apparently are able to protect p against the toxic effect of excess metals without red uptake of the toxic metal by the plant. Thus alum has been found to decrease the toxicity of excess c in citrus plants but does not inhibit the uptake of c by the plants. An increase in the rate of supply of gen, potassium, calcium or magnesium decrease toxic nickel symptoms in oat plants but does not the uptake of nickel (Crooke and Inkson, 1955).

Physical Properties of the Soil

The soil structure is a controlling factor in the tion, drainage and temperature of the soil. The stru is partly dependent upon the size and shape of th particles; soils containing a high percentage of the fractions tend to be compact, to have poor drainag to contain relatively little soil air. Soil temperat affected by the structure, water, and humus conten color of the soil as well as climatic factors. Since tion and temperature affect the rate of minera accumulation in plants and since drainage may affect the local supply of aerated water and metal these physical properties can be expected to infl the metal content of plants.

The size of soil particles, metal content and availability commonly are related. Soil samplin heavy metals (lead, copper, zinc) in northern Sask wan showed a close correlation between clay c and amount of metal; clay soil containing up to 8 as much heavy metal as sandy soil over an unminer area (Byers, 1956). Roberts (1949, p. 73) has the particle size of the soil may correlate with its b content. Soil samples with an average size of 0.0 contained several percent more barium than th 1.65 mm. Barshad (1948, p. 189), working with n denum, reports that particle size has little effect c concentration of this metal in the soil. On the ba 27 samples Lovering and Huff (1950, p. 507) rep average copper concentration at San Manuel of 36 in the silt and clay fraction of the alluvium an ppm copper in the more coarse fraction. Rudrin pp. 19-25) has demonstrated that the fine fracti gray limestone soils contain more phosphorous tha coarse fraction. Since the clay fraction commonly mulates in certain layers or horizons in soils, size s is partly responsible for the uneven distributi trace elements in soil profiles. Without questio greater metal content of clay-sized material mainly from the greater ion exchange capacity in as well as the leaching of metals from more perm sandy soils.

Reitemeier (1946, p. 211) working in arid re has demonstrated the effect of increasing soil moist solubilities of different ions. By increasing the mo in six different soils he found that calcium and n sium increased in four soils and continually dec in one. Chloride and nitrate decreased by 32 to 5 cent on dilution.

The effect of soil moisture on pH is described by Hass (1944, p. 39); he found pH decreased as moisture decreased.

Mitchell (1955, p. 271) has reported a remarkable mobilization of Co, Ni, Fe, V, Cu, and Mn in soils that were very poorly drained. Several times as much metal was extracted by 2.5 percent acetic acid or neutral normal ammonium acetate from poorly drained soil. Fujita and Sherman's work (1948, p. 144) with manganese showed that this metal is released by a waterlogged soil, reduced by a damp soil and released by a dry soil. Increased solubility of molybdenum, silver and lead is observed in other poorly drained profiles. The cause of this mobilization is probably chemical though it is also known that repeated and intensive drying of clay soils increases their capacity to fix some metals.

Although the magnitude of the effect caused by variations in physical properties of the soil along a traverse is unknown, biogeochemical anomalies that coincide with changes in soil structure or with soil moisture content changes from dry ground to swampy ground should be examined very critically.

Environment

Since photosynthesis controls salt accumulation, it is further likely that plants growing in the shade will absorb different amounts of metals than plants growing in the sun and in the same soil. The uptake of zinc by oats was found to increase with temperature and duration of light (Ferres, 1951). Experiments with Cuban tobacco have shown that these plants accumulate more mineral matter when shaded than when they are in the direct sunlight.

The rate of transpiration or the volume of water absorbed by healthy plants appears to have little effect on the amount of metal taken up though the rise of water in the stems may facilitate translocation of ions and indirectly affect uptake. Uptake of solutes may be more nearly proportional to absorption of water if the active roots are injured.

Lovering et al. (1950, p. 509) report that the amount of precipitation in humid and arid regions influences the accumulation of copper by plants. Roberts (1949, p. 67) working with barium shows this metal is more available to plants in areas of high rainfall than in areas of low rainfall. Low rainfall increases the iron and decreases the manganese in plants (Warren et al., 1952b, p. 12).

The marked variation in metal content of plants from season to season may be in part a result of chemical and physical effects of climatic changes on the soil. The exchangeable copper in a soil was found to vary from week to week, ranging from 46 grams per acre in late June to 107 grams per acre in mid-September, and back to 57 grams per acre in November. The autumn rise was attributed to greater moisture since the soil yielded less copper when dried before extraction. Sherman and Shaner (1943), on the other hand, found more manganese could be extracted from a soil if it were first allowed to dry. Roberts (1949, p. 67) reports no significant correlation between temperature and the amount of barium in the soil. In areas of considerable relief, variations in the weather that produce strong differences in soil temperature and soil moisture content exist and can be expected to affect plant metal content. This may account for the observation of Warren et al. (1952, p. 437) that in many areas the metal content of plants on north and south slopes differs markedly.

Plants showing deficiency symptoms for certain metals sometimes can be "fertilized" by spraying leaves and stems with solutions containing the metal needed. Iron, copper, manganese and zinc are often supplied as sprays and arsenic can be injected from insecticide sprays. It is quite likely that small amounts of metal carried from smelters or from ore dumps by the wind as fumes or as dust could accumulate in plants in this way. This might result in a misleading anomaly even though the plants are thoroughly washed prior to ashing and analysis.

Summary

The exchange capacity and the energy with which ions are bound will largely determine the amount of metal taken and retained by the soil from soil solutions or from solids. These may be major factors, then, in establishing or preserving anomalously high metal contents in soils over ore bodies. Not much is known about the exchange relations between soil materials and metals present in minor amounts. Field data mentioned above suggest that variations of a few fold in metal content of the soil can occur solely because the clay or organic content of the soil changes markedly. Several successful trials of soil sampling over known ore bodies indicate that in these cases at least the excessive amount of metal ions in soils over the ore was sufficient to blanket effects due to variations in the soil alone. Nevertheless variations in soil metal content that coincide with obvious changes in soil conditions, such as clay or organic content would need to be interpreted cautiously.

The metal content of a plant growing on these soils is dependent upon the availability of the metals to the plant. Because plants obtain the metals very largely through the base exchange properties of their own roots they must compete with other exchange materials and absorbents in the soil and with other plants and microorganisms for these metals. Those exchange materials in the soil that have a high binding energy for a given cation also release that cation less readily to plant roots. Quantitative data here are also very sparse. Chemical extraction of metals from soil by leaching with dilute acetic or hydrochloric acid, neutral normal ammonium acetate, hot water and other solvents is commonly used to get an indication of the availability of metals to plants. The method is not entirely satisfactory. On the basis of such extractions, for example, there is commonly a large overlap in apparent availability between soils that are deficient and soils that are adequate in some nutrient metals.

The effect of the presence of other ions is too complex and too variable between kinds of plants to permit much generalization. Cases were mentioned above where the presence of one metal caused the uptake of another to change by as much as ten fold. The strange correlation of the ratio of copper to zinc content of plants with mineralization in cases where neither the copper nor the zinc alone correlated reported by Warren et al. (1949) and White (1950) is probably a manifestation of similar metal relationships.

Because the main purpose of biogeochemical prospecting is to obtain a cheap and rapid indication of possible mineralized areas it is hardly practical to make an extensive soil survey for variations in the many complicating factors. In small areas the variations may be insignificant. Attention can be given to the physical condition of the soil and also to the bedrock. Limestone and dolomite are important in that they contain the carbonate ion. This ion may alter the pH of the soil or the carbonate radical itself may enter into chemical reaction with the metal sought. Riddell (1952), working in limestone terrain on the Gaspé Peninsula, reports zinc salts form soluble carbonate compounds, while copper and lead form insoluble compounds. The influence of a high percentage of carbonate may have been responsible for the apparent inactivity of copper and lead in the limestone terrain of the Tri-State district. Harbaugh (1950, p. 563) testing for zinc, copper, lead, tin, nickel, cobalt, and silver, reported only zinc showed any significant variation from place to place over the mineralized area.

The chemical effect produced by serpentine parent rocks has been discussed by Walker (1948, p. 475). In the three principal serpentine soils tested, molybdenum was deficient in that it was unavailable to plants. This relationship has been discussed under ion exchange above.

In areas where evaporates predominate care should be taken in evaluating biogeochemical results for certain metals. Riddell (1952, p. 184) suggests sulfates of zinc and copper are highly soluble while lead sulfate is insoluble in ground waters associated with these deposits. Barshad (1951, p. 387) has shown that sulfate decreases the solubility of molybdenum. Fujimoto (1948, p. 132), working with manganese, reports large amounts of chlorides release this metal in the soil. Sodium-salts tend to mobilize copper by a dispersive effect with the acetate more active than the chloride (Jamison, 1942, p. 297).

It is reasonably certain that the choice of plant and plant organ sampled will not materially affect the pattern of a biogeochemical anomaly provided that the variation in soil metal content is large and that the same organ and plant are sampled throughout the survey. The survey should be completed within a few days. It should be remembered also that biogeochemical prospecting is a cheap and rapid adjunct to other techniques. We doubt that a variation of only two or a few fold in the metal content of plants is sufficient in itself to justify expensive exploration. The anomaly should first be checked through sampling other kinds of plants, through sampling the soil or through use of other geological and geophysical techniques.

BIOGEOCHEMISTRY OF MOLYBDENUM

Molybdenum, which is not found in the native state, occurs in thirteen minerals, the most important of which is the sulfide, molybdenite. Molybdenite is genetically associated with late acid igneous rocks, in granites, pegmatites and aplites. It is known to be found in contact metamorphic deposits and in fissure veins, in both deep-seated and near-surface deposits. Molybdenum is associated with cassiterite, scheelite, wolframite and fluorite in vein deposits, and with lime silicates, scheelit chalcopyrite in contact metamorphic deposits.

Table 6. Molybdenum in soils.

Number of soils tested	Location	Range	Average	Reported by
20	California	0.1 — 9.7	2.01	Barshad
--	Wyoming	0.08—20.0	--	Stanfield
18	New Jersey	0.8 — 3.3	1.99	Evans and Purvis
79	Hawaii	7.9 —73.8	25.8	Fujimoto and Sherman
6	Hawaii	18.6 — 1.8	9.1	Edgington
20	Europe	4.3 —69.0	27.8	Bertrand
8	France	1.0 — 0.3	0.5	Edgington
--	Russia	-- — --	2.6	Vinogradov and Vinogr
187	Argentina	-- —24.0	2.0	Trelles and Amato

Data from Robinson and Alexander (1953)

Molybdenum ranks 34 in relative abundance the elements. Sea water contains but a fraction (0 of a part per billion of this metal as do many waters. The average molybdenum content of the crust has been reported to be 10 ppm by Fersm quoted in Wells (1937). However, Rankama and S (1950) have recently placed the average for th ment between 2.5-15 ppm while Mason (1952, believes 15 ppm is nearer to the true average. In g soils contain from one part per billion to a few per million molybdenum. Robinson et al. (1951, p report that average United States soils range fr to 3.5 ppm molybdenum. The same authors sho the average molybdenum content of 500 soils fr United States, South Africa, Alaska, Hawaii, Rico and Australia is 2.3 ppm (Robinson and Alex 1953, p. 288). This result combined with the res 237 Argentinian and Russian soil analyses giv average of 2.5 ppm molybdenum; Barshad (195 ported a soil range of 0.8 to 10 ppm. While the denum concentration of some soils may reach man of ppm in certain areas of the world (Hawaiian contain as much as 73.8 ppm), the average for all s probably below 10 ppm (Robinson and Alexander, p. 288). The accompanying table shows the molybd content of soils from eight widely separated area

Kuroda and Sandell (1954) give the following age concentrations of molybdenum in various granitic rocks 1.1 ppm; basalts and diabases 1.1 gabbros 0.6 ppm; ultramafic rocks, including 9 s tines, 0.5 ppm; organic-poor shales, 1 ppm; lime and dolomites less than 0.5 ppm.

Plants and animals require molybdenum for n life processes as this metal functions as a cataly regulating the complex chemical reactions that place in living cells. A deficiency of molybdenu plants produces a variety of effects, the most comm which is yellowing leaves and failure to produce fr conditions that can be corrected by adding trace am of molybdenum to the soil. Leaves of the lemon were demonstrated to be normal when they cont more than 0.24 ppm of molybdenum but those co ing 0.01 ppm were deficient; a lower limit of 0.01 below which plants exhibit malnutrition effects has determined. The essential role that molybdenum in plant nutrition has been demonstrated by workers including Arnon and Stout (1939) and

1941). The effect of molybdenum in plant growth shown in legumes in which it accelerates nitrogen ion by bacteria. In Australia the application of late to soils increased the yield and nitrogen con- legumes, but nonlegumes showed no change ffer and Linz, 1952, p. 112).

ough the necessity for molybdenum in plants has stablished, there is much less agreement among s with respect to toxicity resulting from high con- tions of this element. Killeffer and Linz (1952, 1) stated that excessive amounts of molybdenum injure plants. On the other hand Barshad (1948,) believed molybdenum has no apparent toxic Barshad's conclusion is supported, at least for trations of less than 300 ppm, by the high molyb- content of many plants: corn 46.8 ppm, alfalfa pm, sunflower 15.9 ppm, tomato 34.0 ppm, and s 281.0 ppm, none of which exhibited toxic symp- Stiles (1946, p. 134) reported the following molyb- concentrations in different plants: clover 156 imothy 30 ppm, rye grass 54 ppm, and Yorkshire 8 ppm.

minor amounts of molybdenum are required for hy plant; but many plants concentrate this metal h as a thousand fold from the soil in which they (Killeffer and Linz, 1952, p. 112). Lewis, as re- by Stiles (1946, p. 134), showed clover, a member legume family, assimilated more molybdenum than er plants by ratios of as much as seventeen to one an average of by five to one.

shad, working with 22 plants in soil of pH 8, has strated that there is a difference between total lenum content of the soil and the fraction that lable to the plant (average ratio 2:1). Further, ws the accumulative powers of those plants in great quantities of molybdenum when the soil s but minor amounts.

Average molybdenum content of plants as related to molybdenum content of soils.

PLANT[2]	Concentration*					
Mo	10	5	4	1.5	0.5	trace
ble[1] Mo	6	3	2	0.8	trace	trace
ericana	220	--	--	--	--	--
hespida	200	100	54	36	8	0.8
niculatus	150	40	47	16	11	4
repens	150	80	50	12	5	3
fragiferum	--	--	50	12	5	4
subterraneum	175	50	--	--	--	--
alba	80	30	77	18	22	5
officinalis	80	28	55	14	5	2
indica	80	50	30	15	13	7
sativa	30	15	16	13	5	1.3
vulgare	27	--	--	--	--	--
tiva	21	5	7	6	4	2
n vulgare	18	17	--	--	--	--
yana	40	14	13	5	--	--
erenne	33	10	18	7	4	2
latior	--	--	7	2	--	--
glomerata	--	--	9	5	--	--
dilatatum	9	2	4	2	--	--
vulgare	7	2	--	--	--	--
dactylon	11	3	7	4	--	--
halepense	5	--	--	--	--	--
cicutarium	--	--	13	2	--	--

Modified after Barshad (1951)

pp dry matter; first one foot of soil.
ou of total soluble at pH 8.
du cate; stems and leaves.

Background values have to be determined in barren areas for each biogeochemical study. However, certain tentative limits have been established for molybdenum in plants by Barshad and by Robinson. Barshad's values range from a trace to 220 ppm; Robinson gives a range of a trace to 137 ppm. In general the average will be below 100 ppm and in most cases above 10 ppm.

As a general rule, analyses of most plants growing in soils containing high concentrations of molybdenum will show a biogeochemical anomaly. However, the lesser plants, especially the legume family, reflect the soil concentration most effectively. The following plants are well suited to biogeochemical prospecting and have been used successfully in molybdenum studies:

Table 8. Plants useful in prospecting for molybdenum.

Coreothrogyne filaginifolia (Wooly aster)
Devils paint brush
Vicia americana
Medicago hespida
Lotus corniculatus
Trifolium repens
Trifolium fragiferum
Trifolium subterraneum
Melilotus alba
Melilotus indica
Melilotus sativa
Triticum vulgare
Avena saliva
Horedum vulgare
Chloris gayana
Lolium perenne
Cneoridium dumosum
Quercus weslenzenii (Interior live oak)
Quercus douglasii (Blue oak)

Misleading Anomalies

Exchange Material pH, and Other Ions. As the pH and exchange material in the soil are closely related, they have a combined effect on the availability of molybdenum to plants.

Clay is the most common and effective exchange material in the soil. It is possible that clays, through differential absorption, may nullify the effect of a large concentration of molybdenum in the soil. The amount of absorption depends primarily on the soil pH and secondarily on the type of clay. Organic exchange materials become important only when the organic content of the soil is abnormally high. An accompanying figure, taken from Barshad's studies with molybdenum, illustrates the relationship between pH, clay type and availability of molybdenum to plants.

The pH controls molybdenum availability through its effect on solubility and through its effect on absorption of molybdenum by clay minerals.

The solubility of molybdenum minerals increases directly with decrease in pH of the soil solutions. As the molybdenum minerals near an ore deposit have not completely lost their identity, much of the soil molybdenum will be in the mineral form. The acid conditions common near ore deposits may, however, promote the decomposition of the mineral compounds to release the molybdenum. An accompanying table illustrates the solubility of molybdenum minerals in water, sodium hydroxide and hydrochloric acid.

Once freed from the other elements in the mineral compound, molybdenum forms complex ions with oxygen, the most common of which is the divalent oxide

Table 9. Solubility of molybdenum minerals in various reagents. (Mo in ppm)

Reagent	Molybdenite MoS_2	Ferrimolybdite $Fe_2(MoO_4)_3 \cdot 7.5H_2O$	Wulfenite $PbMoO_4$	Molybdic oxide MoO_3
H_2O	0.05	5.4	0.014	250
0.1N Na(OH)	0.44	88.0	27.4	Very sol.
0.1N HCl	2.84	168.0	3.0	130

After Barshad (1951)

$MoO_4^=$. It is at this point in the chemical history of molybdenum ions that they are likely to be absorbed by the clay fraction of the soil. Barshad (1951, p. 299) stated that soil molybdenum is in three forms: (1) as a soluble molybdenum salt, (2) as a component of soil organic matter, and (3) as the absorbed exchange anion $MoO_4^=$. The newly formed complex ion is of such size that it can enter into exchange relationships with the OH radical in the clay fraction of the soil. There is a potential set up between the OH ions in the clays and the molybdenum complex which favors exchange and is governed by the pH. To illustrate this, Barshad (1951, p. 298) has shown that a removal of molybdenum from acid clays results in an increase in pH. The greater the pH, the smaller the amount of molybdenum absorbed into the crystal lattice of the clay until at pH 7.5 virtually no molybdenum is absorbed (Barshad, 1951, p. 298). Therefore, only in alkaline soils does this ion become available to plants in any significant amount.

Table 10. Relationship of molybdenum in plants to soil pH.

Plant	pH range	Increase of Mo in plant (ppm)
Ladino clover	5 to 7	10
Ladino clover	5.3 to 7	66
Ladino clover	6 to 7	58
Ladino clover	5.3 to 7	39
Ladino clover	5.3 to 7.5	26
Lotus corniculatus	5.7 to 7.5	96
Lotus corniculatus	5.3 to 7.5	74
Rhodes grass	7.3 to 7.9	15
Rye grass	7.1 to 8.5	—3

After Barshad (1951)

The work of Evans, Purvis and Bear (1951, p. 118) on alfalfa in New Jersey's Nixon loam demonstrated that the molybdenum concentration in alfalfa increased with higher pH. Their results are shown in an accompanying figure, and show clearly the changes in concentration with increase in pH.

When the pH exceeds 7.5, molybdenum is again absorbed but in smaller amounts. An accompanying table shows the reabsorption of molybdenum in the alkaline range as well as the general increase of alkalinity with depth shown by most mature soils. The concentration of molybdenum at the surface could also be attributed to enrichment by many cycles of plant growth which absorbed molybdenum and subsequently contributed it to the surface soil layer after death.

Walker (1948, p. 475), working with the serpentine soils of northern California, has shown these soils to be abnormally low in available molybdenum. He believed this to be a general condition of all primary soils derived from serpentine parent material. He thought it to result partly from the inherently low molybdenum content of serpentines; it may also result partly from the fi of molybdenum in clay molecules. Clays derived serpentine rocks are high in magnesium, a metal chemical activity and ionic radius are similar to n denum.

Table 11. Relation of available molybdenum to pH at d

Soil type	Depth (inches)	pH	Available molybdenum (i
Sandy loam	0-12	7.3	3.3
	12-24	7.9	2.6
	24-36	7.4	2.1
	48-60	8.1	1.8
Clay loam	0-12	7.3	6.8
	36-48	8.7	5.8
	48-60	9.1	3.0
Clay loam	0-12	7.5	2.9
	12-24	7.2	2.5
	36-48	6.8	1.3

Modified after Barshad (

Table 12. Some ions that affect the uptake of molybdenum by plants.

Ions that stimulate the uptake of Mo	Ions that suppress the uptake of Mo
PO_4	CO_3
Cl	HCO_3
NO_3	OH
	SO_4
	S
	N
	FeO

Compiled from several sources.

Changes in the chemical makeup of soil are di to recognize in the field. Only under optimum cond is it possible to correct errors that are the result lack of knowledge of the exact soil chemistry. O the most common sources of change in the ionic con tion of the soil is due to a change in underlying type, and the investigator who crosses a contact bet two rock types without recognizing it may recor anomaly where none exists. There are many rocks could introduce sufficient foreign ions to produce a misleading anomalous effect; some of these are in an accompanying table.

Table 13. Sources of detrimental ions.

Rock type	Ion supplied to the
Limestone and dolomite	CO_3, HCO_3
Playa deposits (salines)	SO_4, Cl, OH, N
Basalt	PO_4
Gossan	S, SO_4

Season. Plants, as the result of cyclic chang their physiology, contain different amounts of mi material during different times of the year. The change in the assimilation of molybdenum by plant been studied by Barshad; his results are summariz the accompanying table. This cyclic change with re to molybdenum as reported in the lesser plants i reflected in deciduous trees.

Age of the Plant and Organ. As the plant deve certain chemical and physical changes take place v alter the amount and kind of material that the will require from the soil. Similar changes are rep in the development of each organ.

...e 14. Effect of season on molybdenum content of plants.

Plant	Location*	Molybdenum in leaves		
		Spring[1]	Summer[2]	Fall[3]
...fa	Coloma	16.0	20.0	28.4
...fa	Buttonwillow	9.2	11.3	18.0
...lo... alba	Pond	--	32.0	77.5
...do... alba	Greenfields	18.1	44.8	--
...rniculatus	Greenfields	30.0	43.6	92.9
...rniculatus	Wasco	20.6	31.0	72.0
...grass	Buttonwillow	8.1	14.0	25.0
...s	Greenfields	2.5	4.3	6.5
...s	Shafter	4.3	7.5	10.0
...grass	Pond	1.7	5.0	--
...grass	Shafter	3.6	4.9	9.8
...ass	Buttonwillow	3.9	--	8.2
... grass	Greenfields	4.0	--	7.6

After Barshad (1951)
...Kern County, California.
...ay.
...ly.
...er-October.

...t s necessary, therefore, to sample growth of the ...eage. Second year stems and leaves have proven ...the most satisfactory.

...nslocation. After absorption by the root system, ...utrient materials are transported to different parts ...plant structure. Molybdenum, as evidenced by ...diographs, moves directly into the interveinal ...s of new leaves in most plants (Stout and Meagher, ...p. 473). In legumes, accumulation is centered at ...ed pods (Killeffer and Linz, 1952, p. 112). Stout ...Meagher (1948, p. 437) state that molybdenum is ...sorbed in the stems of plants to any large degree, ...arshad found, after testing 14 plant types and 34 ..., the highest molybdenum concentration was found ...in the leaves of 16 of the plants, in the stems of ...d in the roots of four.

Field Studies

...ee areas in California were studied to determine ...biogeochemical prospecting can be used to indicate ...mally high concentrations of molybdenum in the ...Factors (reported in the agricultural literature) ...nfluence the concentration of molybdenum in soils ...plants were observed in the field and their impor... to biogeochemical prospecting evaluated. Molyb...n, in the minerals molybdenite or powellite, was ...n to be present in all areas. In all but one area ...etal was concentrated in definite zones. The plant ...e soil, geology, climate, and topography differ ...y in the three areas.

...ecimens of several species of trees and smaller ...s were collected. At certain stations old and new ...h was collected for comparison, as were different ...s of the same plant. In each area soil samples ...taken where feasible and the pH determined. The ...ipal clay in the soil at the Bour molybdenum mine ...dentified by X-ray methods and its concentration ...lated. Molybdenum concentration in the soil in ...area was also determined.

...o methods of plant analysis were used in these ...es. Quantitative spectrographic methods were used ...alyze samples collected at the Bour molybdenum mine, whereas a wet chemical technique, developed by the U. S. Geological Survey, was used to analyze the samples from the other two areas.

Table 15. Variation of molybdenum content of plant leaves of various species.

Plant	Milligrams of Mo per kilogram of dry matter
Desert athel (tamarisk)	34.0
Black locust	15.9
Eucalyptus	1.4
Cottonwood	1.6
Yellow sweet clover	59.3
Cowpeas	141.0
Alfalfa	20.7
Perennial rye grass	11.6
Tall fescue	14.9
Prairie brown grass	8.7
Wheat stubble	26.4
Sweet corn	46.8
Mullet	50.4
Sunflower	15.9
Watermelon	14.1
Cantaloupe	1.3
Tomato	34.0
Malvarotundifolia	66.0
Cotton	21.6
Romie	11.8

After Barshad (1951)
All grown in Merced clay loam, Buttonwillow area, Kern County, California. Surface foot contained 6 mgm of Mo/Kgm. pH 7.2.

Areas for study were chosen where diverse soil, plant, and climatic conditions could be expected. These areas demonstrate, to a limited degree, the variation in results that can be expected when prospecting for molybdenum using biogeochemical techniques.

Bour Molybdenum Mine

At the Bour molybdenum mine, 6 miles west of Ramona, San Diego County, California, molybdenite is disseminated as flakes in a northwest-trending aplite dike that cuts the Cretaceous Woodson Mountain granodiorite. The ore is reported to average 0.5 to 1.0 percent molybdenite. The dike ranges from 30 to 300 feet in width. A 240-foot adit driven from the northeast intersects the dike 200 feet below the surface. Two open cuts are south of the adit.

Two biogeochemical traverses were made across the dike; one 260 feet long, bearing N. 68° E., was 300 feet south of the adit; the other, 135 feet long, bearing N. 80° E., was 700 feet south of the adit and entirely within the dike. The samples were collected in February 1954.

Biochemistry. Leaves and stems of *Cneoridium dumosum* were collected at each station. This plant, which is widely distributed throughout the region, is more abundant on the granodiorite, where a deeper soil is developed, than on the aplite dike. No attempt was made to sample only the youngest growth, as new growth was not obvious. The plant was in bloom at the time of sampling.

Soil samples were collected at all but three stations. About 1 pound of soil was collected from 3 inches below the surface. No true soil profile is developed anywhere in the area, and existing soil forms only a thin veneer in protected depressions. The aplite dike, being more resistant to erosion, stands above the country rock and is almost devoid of soil.

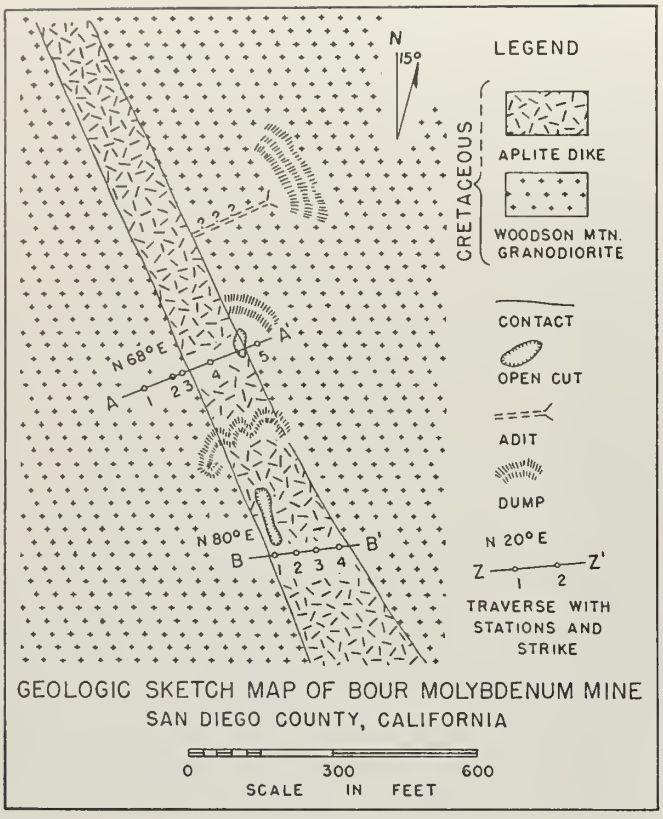


FIGURE 6.

Analysis. The plant and soil samples were analyzed in accordance with procedure outlined by Nichols and Rogers (1944). The plants were dried overnight at 100° C., ground in an agate mortar, then ashed in a pot furnace at 450° C. for 2 hours. Silica crucibles were used to avoid salting the samples. Suitable molybdenum standards were prepared with beryllium added as an internal standard, and a working curve was developed. Twenty mg. samples of ash were ignited between carbon electrodes in a D.C. arc using a 4mm. gap at 15 amps. Spectrographs were obtained on a Jarrell-Ash 3.4-meter Wadsworth-mounting grating spectrograph. Line transmission was measured on a Jarrell-Ash microphotometer, converted to line intensity, and the molybdenum content of the ash obtained to the nearest 10 ppm by comparison with the working curve. The molybdenum line at 3170 Å was used for comparison.

The soil was ground and analyzed in 100 mg. samples in the same manner as outlined for the plants. A determination of soil pH was made in accordance with the method outlined by the Soil Survey Manual of the Department of Agriculture (1951, p. 237). A 1:1 ratio of soil to water was shaken vigorously and allowed to stand for 30 minutes, reshaken and checked with a pH meter. The soil pH was slightly acid in all cases and varied only by one full unit. X-ray analyses determined the principal clay mineral present and the relative amounts in each sample.

Results. The results of plant analysis show a definite anomaly over the metalliferous dike. Background values average 15 ppm molybdenum in the plant ash (Stations

Bour molybdenum mine, San Diego County, Californi

	Traverse A-A′					Traverse B		
	Station					Station		
	1	2	3	4	5	1	2	
Molybdenum concentration in *Cnearidium dumosum* (ppm)	10	20	150	200	10	200	200	1
Molybdenum concentration in soil	10	20	20	no soil	10	140	no soil	
pH of soil	6.00	6.50	6.90	no soil	5.90	6.10	no soil	6.
Relative concentration of illite in soil (percent)	70	100*	60	no soil	90	85	no soil	

* Standard (100 percent).

1 and 2, traverse A-A′). At Station 3, which v feet from the dike, the concentration reached 15 and at Station 4, near the center of the dike, the denum concentration rose to 200 ppm, falling off to 10 ppm at Station 5, some 50 feet beyond the

The molybdenum concentration in the soil sho similar but weaker anomaly over the ore body. mum concentration was 120 ppm over background imum concentration 10 ppm, in the six soil sample lyzed. On the average the plant samples taken ne ore body contained 100 ppm more molybdenum ash than did the soil samples.

The soil pH ranged from 5.9 to 6.9 and had apparent effect on the molybdenum anomaly. The cipal clay mineral present in the soil was illite. It markedly in concentration; the highest value w corded at Station 2 along traverse A-A′ and the trary value recorded at that station was taken standard (100 percent). The lowest concentratio 17 percent of the standard; all other concentration above 50 percent. Like the soil pH, the clay cont the soil had no apparent effect on the anomaly high concentration of molybdenum may have sat the exchange material in the relatively small volu soil, rendering this effect negligible. Howeve slightly acid condition of the soil may have inc the exchange capacity of the illite and lowered t tensity of the anomaly.

Cosumnes Mine

The Cosumnes mine, 15 miles southeast of Place El Dorado County, in section 25, T. 9 N., R. 12 E. is on the Middle Fork of the Cosumnes River i central foothills of the Sierra Nevada.

Mineralization is along the periphery of an ig body which intrudes metasedimentary rocks of the veras group. Molybdenite occurs in minor amou flakes from one millimeter to a centimeter or m greatest diameter. Copper, lead, silver, and gold mi are also found with the molybdenite, which is n northeast-trending quartz vein and contact metam zone.

The oldest rocks in the area are the metasedi of the Carboniferous (?) Calaveras group compos a quartz-biotite-muscovite schist and recrystallized

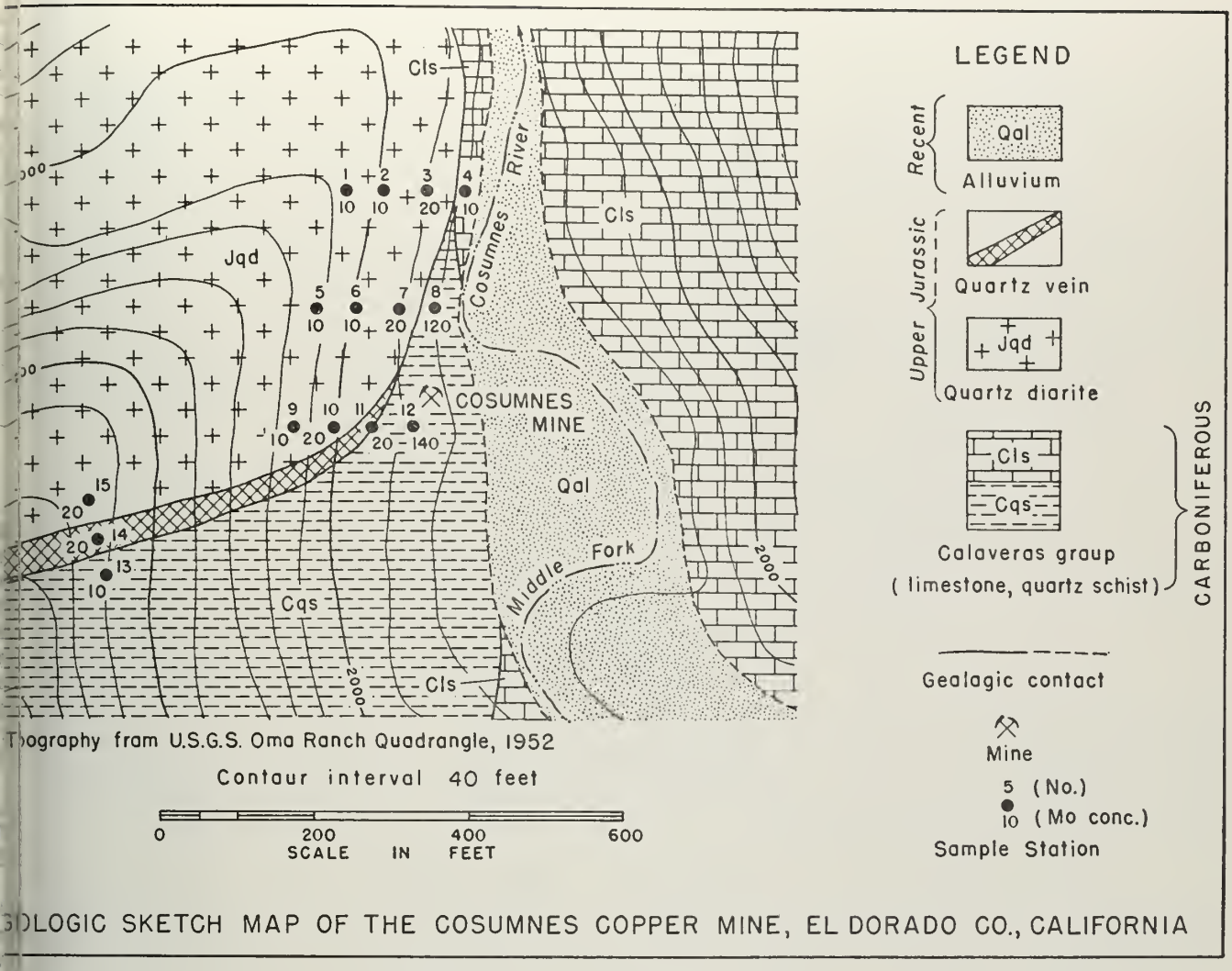


FIGURE 7. North is toward top of sketch.

Intrusive into these rocks is a biotite-hornblende rt diorite of Upper Jurassic age. A contact meta-pic zone is developed along the southwest contact wn the quartz diorite and schist. Massive grossu-te and epidote are common in this zone. A quartz to 15 feet wide follows the igneous-metamorphic ta and thin veins have invaded the contact zone gninor fractures. Molybdenite was not observed in qurtz vein on the surface, being confined principally he contact zone.

h mine has been developed along the quartz vein by aits driven from the east and a small open cut at srface. Two large dumps attest to considerable in activity.

ichemistry. Soil samples and leaves and twigs of r r Live Oak (*Quercus weslenzenii*) were collected 15 stations in the mine area, and at one station 2 s istant for a background sample. The samples were e d on a grid pattern with the stations spaced 50 art in an east-west direction and 150 feet apart enerally north-south direction. A short traverse a o made across the quartz vein. An effort was made o ct only young growth, but not current growth, from trees of approximately the same age. The Interior Live Oak is abundant around the mine and little difficulty was experienced in selecting suitable samples. A deep soil covers the quartz diorite and schist but cover on the limestone is scant and there is none on the quartz vein near the mine. About 1 pound of soil was collected 6 inches below the surface at each station. Eleven of the stations were located on the quartz diorite, three on schist, one each on the limestone and quartz vein. The samples were collected in November 1954.

Analysis. The plant samples were analyzed by a wet chemical technique developed by the U. S. Geological Survey (Reichen and Ward, 1951). Only the leaves were analyzed. The plant material was dried at room temperature for several weeks, then ashed in silica crucibles over a low bunsen flame for 1 hour. A 10 mg. sample of ash was fused with lithium nitrate to destroy the carbonaceous material; the fusion was dissolved in HCl, neutralized, and reacidified. Potassium ferrocyanide and a saturated solution of stannous chloride were added. The solution was shaken with peroxide-free isopropyl ether to abstract the molybdenum complex into the ether layer. Suitable standards of molybdenum were prepared from

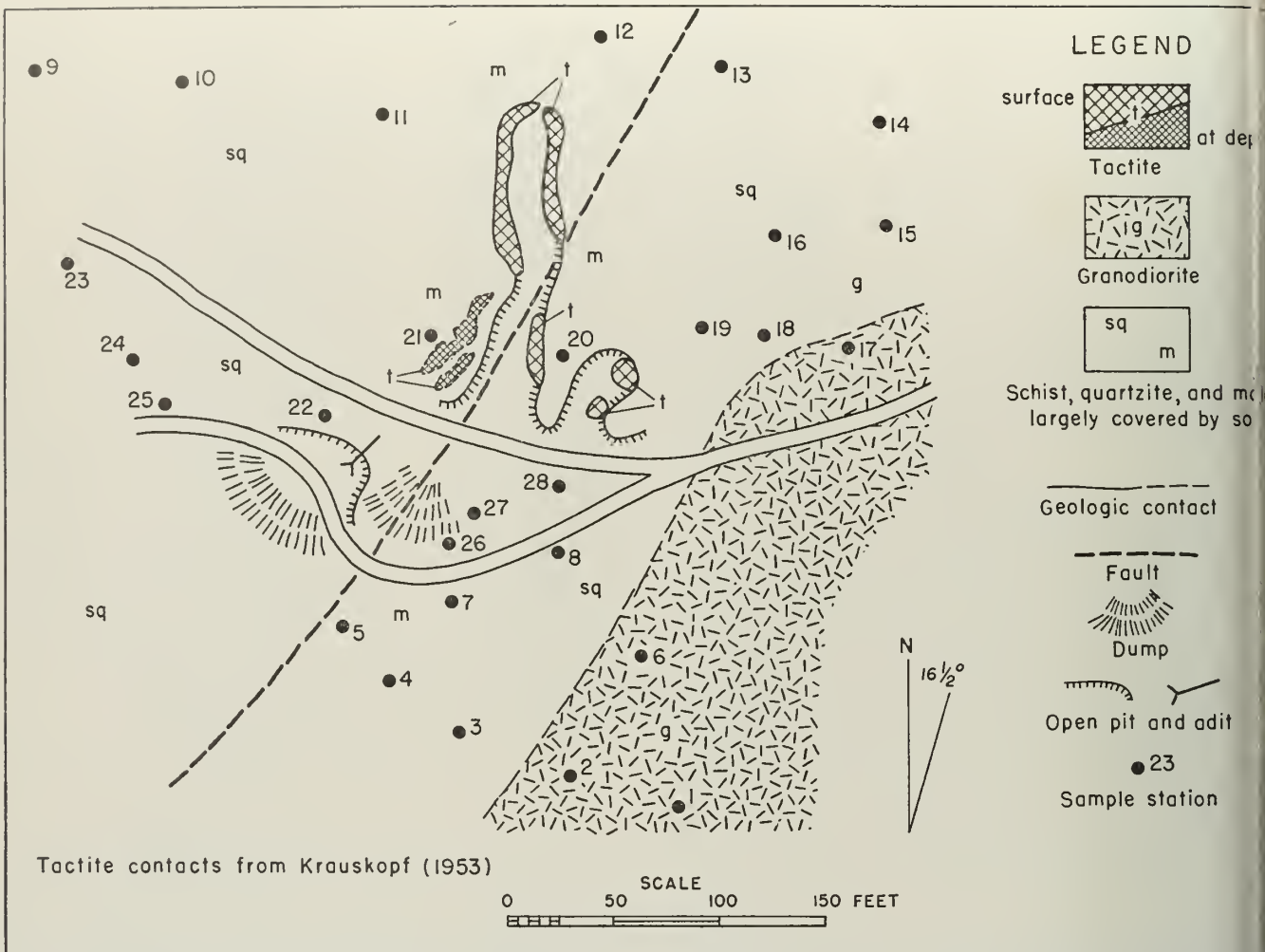


FIGURE 8.

a 0.002 percent molybdenum solution of molybdic oxide. The concentration of molybdenum in the unknown samples was determined to the nearest 10 ppm. by colorimetric comparison with the standards.

The pH of the soil samples was checked in accordance with the procedure outlined by the U. S. Department of Agriculture (Soil Survey Manual, 1951, p. 273).

Results. The concentration of molybdenum in the tree samples increased near the mineralized zone from west to east. Concentration in samples collected over the quartz diorite doubled over the background (10 ppm) while concentration in samples from the schist increased 12 to 14 times over the values recorded on the quartz diorite. There was no significant increase in content in the trees growing on the quartz diorite from north to south. The principal center of molybdenum concentration appears to be in the contact metamorphic zone rather than the quartz vein. This relationship is in keeping with the field observations. A short traverse over the quartz vein, where it was hidden by a deep soil cover several hundred feet west of the mine, showed no anomalous increase in molybdenum.

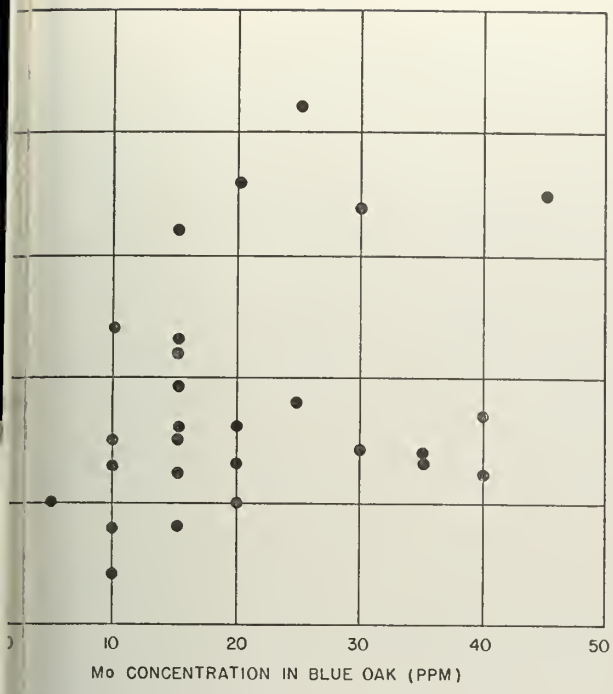
The soil pH was higher in soil samples collecte the quartz diorite than over the other rocks. It r from 6.25 to 7.00 on the quartz diorite and from 5 6.20 on the other rocks.

The pH could not be shown to have a consistent on the availability of molybdenum to the plant sample collected on the soil with the lowest pH contained the highest concentration of molybdenun ppm) which is contrary to what might be exp Moreover, the second highest molybdenum concent (120 ppm) was recorded from a tree rooted in soi a pH of 6.20.

Tyler Creek Mine

The Tyler Creek tungsten mine (west workin sec. 35, T. 23 S., R. 30 E., MD., is 2 miles west o fornia Hot Springs, Tulare County, California, elevation of 3000 feet.

The tungsten mineralization is localized along a zone that cuts a roof pendant of schist, quartzit limestone probably of the Kaweah series (Trias and granodiorite (Jurassic ?) country rock (D



IE 9. Graph showing absence of clear relationship between
:o entration of molybdenum in Blue oak trees and soil pH.

;Krauskopf, 1953). Scheelite and powellite are
ıdin the pendant along a discontinuous tactite zone
el strikes generally northeast. The ore is reported
.v age 0.77 percent WO_4 over the mineralized area;
ctl samples assayed 29 percent. The scheelite con-
ıs dmixed powellite in sufficient amounts (probably
at than 0.4 percent) to draw penalties at the
lt (Jess Acker, lessee, personal communication,
5)

h mine has been worked principally along two adits
ıe large and two small open cuts. Several dumps
ant to the workings and three unimproved roads
e considerably disturbed the natural setting. The
es situated about 150 feet above Deer Creek on a
uth-sloping hillside.

ii eochemistry. Samples of the previous years'
w of Blue oak (*Quercus douglasii*) twigs were col-
ect at 30 stations and leaves and twigs of California
ke (*Aesculus californica*) were collected at Station
t Stations 2, 3, and 27 current growth of Blue oak
s were collected for comparison with the previous
s growth; at Station 11, leaf samples from the
vius years' growth were collected for comparison
ı wigs. Two background samples were collected; one
ı a quarter of a mile (Station 29) and another about
ıla mile (Station 30) from the mine, both from trees
wig in soil overlying granodiorite. Samples were
ı from trees of about the same age (1 foot in trunk
n er). The trees were almost devoid of leaves—only
v from the previous year, and incipient growth from
errent growing season—were present. The Blue oak
ıiformly distributed over the mine area. The sam-
ere collected in April 1955.
t each of the 30 stations about half a pound of soil
ollected from 6 inches below the surface. A well-developed soil, 4 feet deep in some places, covers the greater part of the mine area.

Twig and leaf samples were analyzed in duplicate for molybdenum by the wet chemical technique developed by the U. S. Geological Survey (Reichen and Ward, 1951). The samples were dried at 100° C for 8 hours, then ashed in silica crucibles over a low bunsen flame for 1 hour. The balance of the analysis was carried out as previously described and the results are reported to the nearest 5 ppm.

The soil pH was determined by the U.S. Department of Agriculture method.

Abnormal concentrations of molybdenum were found in 13 of the trees sampled in the mine area. The samples ranged from 5 to 45 ppm molybdenum and averaged 20 ppm.

Table 16. Molybdenum concentration in blue oak growing over different rock types.

	Number of molybdenum samples	Concentration (in ppm)	
		Range	Average
Granodiorite	9	5-40	18
Quartzite and schist	13	10-45	19
Limestone	8	10-35	24

Two background samples taken half a mile and three-quarters of a mile from the mine contained 20 and 10 ppm molybdenum respectively, averaging 15 ppm. The seemingly high (20 ppm) value recorded half a mile from the mine may possibly be explained by the dissemination of tungsten minerals in this region and fortuitous sampling over a mineralized zone.

In general, the highest molybdenum values are rather randomly distributed over the mine area. However, there is some suggestion of a trend northeast from Station 5 to Station 16 with values ranging from 20 to 45 ppm molybdenum. The data are insufficient to explain the high molybdenum content recorded from Stations 1, 9, 16, and 18. Seven stations in the mine area show a content of two to three times the average background (15 ppm). The maximum molybdenum concentrations recorded from this area appear low in view of the high concentrations found in the two previous studies (200 ppm, 140 ppm) all with comparable background values. However, Warren et al. (1953, p. 74) report that of 115 samples collected adjacent to or over ore deposits, 67 tree and plant samples ranged from 2 to 5 ppm molybdenum, and 48 tree samples ranged from 43 to 65 ppm molybdenum; background values were 0.1 to 0.5 ppm. The Blue oak may not be as effective in absorbing molybdenum from the soil as other trees. Analysis of comparative samples (twigs) of Blue oak and California buckeye taken from the same station (5) showed that the California buckeye contained 30 ppm molybdenum as opposed to 20 ppm in the Blue oak.

No significant difference in molybdenum concentration in current and previous years' growth was noted from three stations where both were collected for comparison. The sensitivity of the chemical analysis may not reflect such subtle differences in molybdenum concentration (Reichen and Ward, 1951, p. 1).

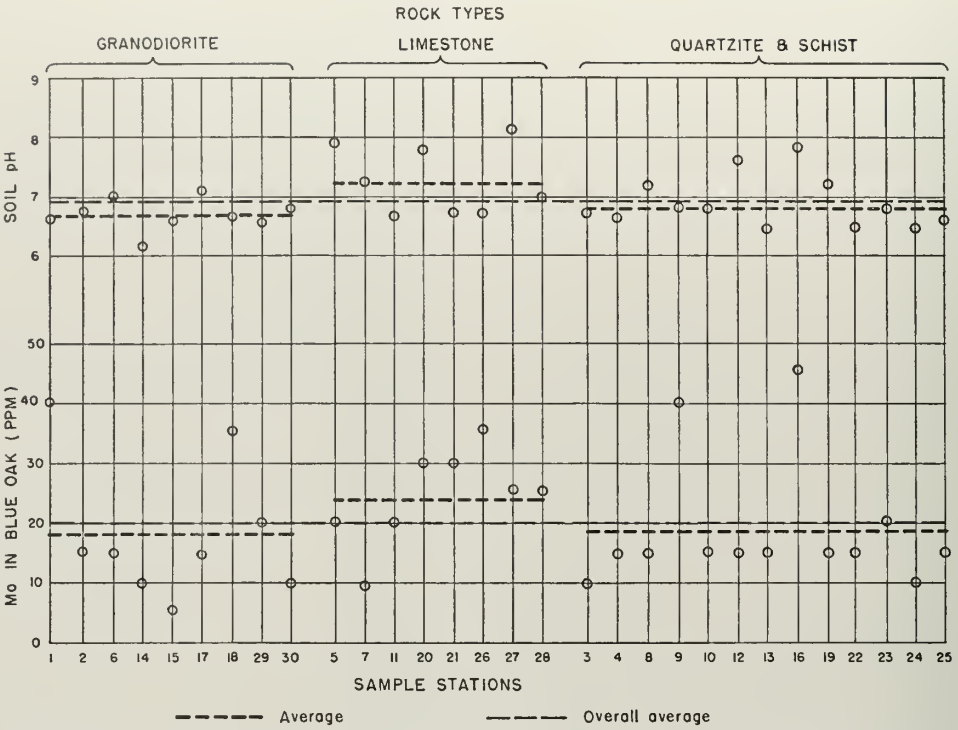

ROCK TYPES
GRANODIORITE
LIMESTONE
QUARTZITE & SCHIST
SOIL pH
Mo IN BLUE OAK (PPM)
SAMPLE STATIONS
1 2 6 14 15 17 18 29 30 5 7 11 20 21 26 27 28 3 4 8 9 10 12 13 16 19 22 23 24 25
Average
Overall average

FIGURE 10. Graph showing concentration of molybdenum in Blue oak trees growing in soils of different pH overlying granodiorite, limestone, and quartzite and schist. The parent rock from which the soil is derived affects the soil pH, which in turn affects the amount of molybdenum taken up by the trees.

Table 17. Comparison of new and old growth.

Station	Molybdenum concentration (in ppm)	
	Current growth	Previous years' growth
2	15	15
3	15	10
27	20	25

Blue oak twigs and leaves of previous years' growth from Station 11 each contained 20 ppm molybdenum.

The soil ranged in pH from 6.20 to 8.10, averaging 6.90 at 30 stations in the mine area. As might be expected, the soil overlying granodiorite was the most acid; the soil derived from quartzite and schist was intermediate; and limestone soil was the most basic.

The discontinuity of the tactite bodies, the movement of soil by creeping, and the disturbance of the ground by mining operations may account for the lack of any

Table 18. The pH of soil overlying different rock types.

Rock type	Number of samples	pH	
		Range	Average
Granodiorite	9	6.21-7.10	6.67
Quartzite and schist	13	6.40-7.75	6.86
Limestone	8	6.65-8.10	7.22

Table 19. Data from biogeochemical survey for moly... Tyler Creek mine, Tulare County, California.

Station	Molybdenum content of Blue oak*	Soil pH	Underlying
1	40	6.60	Granodiorite
2	15	6.75	Granodiorite
3	10	6.65	Quartzite and
4	15	6.60	Quartzite and
5	20	7.80	Limestone
6	15	6.95	Granodiorite
7	10	7.20	Limestone
8	15	7.15	Quartzite and
9	40	6.85	Quartzite and
10	15	6.80	Quartzite and
11	20	6.65	Limestone
12	15	7.60	Quartzite and
13	15	6.40	Quartzite and
14	10	6.20	Granodiorite
15	5	6.50	Granodiorite
16	45	7.75	Quartzite and
17	15	7.10	Granodiorite
18	35	6.65	Granodiorite
19	15	7.20	Quartzite and
20	30	7.70	Limestone?
21	30	6.70	Limestone
22	15	6.40	Quartzite and
23	20	6.80	Quartzite and
24	10	6.40	Quartzite and
25	15	6.60	Quartzite and
26	35	6.70	Limestone
27	25	8.10	Limestone?
28	25	6.90	Quartzite and
29[1]	20	6.50	Granodiorite
30[2]	10	6.75	Granodiorite

* Twigs only (in ppm).
[1] Background sample approximately ¼ mi. from mine.
[2] Background sample approximately ½ mi. from mine.

fi te molybdenum concentration pattern in this area.)ever, as a relatively small area was sampled, it is e that the entire mineralized zone is positive for lodenum and that some factors other than the molyb- nm concentration in the soil have partly determined molybdenum concentration in the trees.

Stce this study was made, the present operators of 'yler Creek mine have driven an adit N. 60° E. for itance of about 300 feet near the former workings. helite mineralization was encountered at depth be- en Stations 20 and 21 where concentrations of 30 n molybdenum were found in the plants. At Station here the highest molybdenum concentration (45 n was recorded in the plants, an ore body was found averaged 0.5 percent WO_3. The total extent of this d is not known; however, it has been exposed for fet in length and 15 feet in width. These discoveries r made without knowledge of the biogeochemical ic.

SUMMARY AND CONCLUSIONS

Biogeochemical prospecting has not developed to the i where its full potentialities can be realized. If this t become a reliable method of prospecting, then cer- refinements in application and interpretation are cssary.

A least 19 factors other than the metal concentra- nin the soil play an important part in determining e metal concentration in plants; at least seven of them e ontrolling factors. These seven are: soil pH, ex- age material, other ions, plant type, age of plant and ga, translocation, and season.

Te field studies reported here provided a means for tg some of these factors. If the effect of one factor tbe separately evaluated in the field, then areas must osen where the other related factors remain con- n.

Te field studies made for this report, made at lo- lies where, as nearly as possible, four of the seven n olling factors were constant, showed that the anom- y etected was due primarily to the high molybdenum ntration in the soil. It was, therefore, a direct fl tion of the underlying ore zone, or was closely lad to it. Additional proof that the underlying ore psit was the responsible factor was provided by soil arses made from samples taken in the Bour mine ic, which showed that the concentration of molyb- nm in the soil fluctuated in the same manner as the ntration of molybdenum in the plants, providing ay identical anomalies. The overall concentration in e oil, however, was lower than in the plants, showing a the plants were a more sensitive prospecting instru- el.

Te data collected at the Cosumnes mine showed con- lable variation in soil pH, and soil ions, which may v been due to the three underlying rock types. The erge soil pH was definitely higher over the quartz o te than over the metamorphic rocks. However, this c r had little apparent influence on the metal con- n of the plants as the highest molybdenum values were c ded from soils with the lowest pH. Molybdenum ntration increased as the ore zone was approached cot at one station where there is some evidence that the suppressing effect of CO_3 and HCO_3 ions, derived from the underlying limestone, reduced the uptake of molybdenum. As at the Bour mine, the high concentration of molybdenum in the soil had a greater effect on the metal concentration in the plants than did the other controlling factors.

More than half of the plant samples collected at the Tyler Creek mine showed no anomalous concentration of molybdenum and there was no uniform concentration pattern related to the ore zone. The data point to the underlying rock type as a principal influence in regulating the soil pH; therefore the rock type might be expected to have some influence on molybdenum concentration in plants. Unfortunately, the data here are insufficient to demonstrate such an influence conclusively. Nevertheless, it will probably be necessary in future investigations to apply a correction factor when traversing from one rock type to another. The anomalous molybdenum content of the plants was considerably lower in the Tyler Creek mine area than at the other two mine areas studied. This may have been due in part to the molybdenum concentration in the soil although, in view of the rather erratic results, it seems likely that the plant type sampled or the high concentration of CO_3 and HCO_3 ions in the soil at certain stations may have reduced the assimilation of molybdenum by the plant. This area then illustrates to a limited degree how the other factors can obscure and disperse a biogeochemical anomaly. The fact that most of the plant samples show a greater than normal molybdenum concentration is evidence that the soil molybdenum concentration is still the principal controlling factor in this area.

Future work in biogeochemistry should be directed toward the accumulation of data on plant-metal-soil relationships for all of the economic metals. The character of the metal as it is related to the soil chemistry and to the geology appears more vital than the influence exerted by the plant. It is true that certain physiological features of plants exert a significant influence in biogeochemistry, but on the whole all plants react with a certain degree of consistency. The important controls lie in the soil chemistry. The behavior of molybdenum is not yet completely understood and there is a real need to extend the studies begun in this investigation. The influence of all the important rock types on molybdenum anomalies would be of interest as would the effect of a wider range in soil pH. More study should be given to the geologic controls. Molybdenum-plant relationships in the vicinity of ore deposits should also be tested under a greater range of climatic conditions.

BIBLIOGRAPHY

Aldrich, D. G., and Terrell, F. M., 1951, Effect of acidification on some chemical properties of a soil and the plants grown thereon: Soil Science, vol. 70, pp. 83-90.

Almond, Hy, 1955, Rapid field and laboratory method for the determination of copper in soil and rocks: U. S. Geol. Survey Bull. 1036-A.

Almond, Hy, and Morris, H. T., 1951, Geochemical technique as applied in recent investigations in the Tintic district, Utah: Econ. Geology, vol. 46, p. 608.

Anderson, Roger Y., and Kurtz, Edwin B., 1955, Biogeochemical reconnaissance of the Annie Laurie uranium prospect, Santa Cruz County, Arizona: Econ. Geology, vol. 50, no. 2, pp. 227-232.

Anderson, Roger Y., and Kurtz, Edwin B., 1956, A method for the determination of alpha-radioactivity in plants as a tool for uranium prospecting: Econ. Geology, vol. 51, no. 1, pp. 64-68.

Arnon, D. I., and Stout, P. R., 1939, Molybdenum as an essential element for higher plants: Plant Physiology, vol. 14, pp. 599-602.

Barshad, Isaac, 1948, Molybdenum content of pasture plants in relation to toxicity to cattle: Soil Science, vol. 66, pp. 187-196.

Barshad, Isaac, 1951, Factors affecting the molybdenum content of pasture plants: I. Nature of soil molybdenum growth of plants, and soil pH; II. Effect of soluble phosphates, available nitrogen and soluble sulphates: Soil Science, vol. 71, pp. 297-313, 387-398.

Beath, O. A., 1937, The occurrence of selenium and selenium vegetation in Wyoming: Univ. Wyoming, Agricultural Experiment Station, Bull. 221, part 2, pp. 29-63.

Billings, W. D., 1950, Vegetation and plant growth as affected by chemically altered rocks in the western Great Basin: Ecology, vol. 31, pp. 62-74.

Bobrowski, Wladislaiv, and Piechota, Aleksander, 1949, Influence of the substratum on the occurrence of heavy metals in the bark of contemporary pines on the Triassic of southwestern Poland: Panstwowa Sluzba Geol. Panstwowy Inst. Geol. Serv. geol. Pologne, Inst. geol. Pologne Biul. 58, pp. 6-12.

Bolle Jones, E. W., 1955, The effect of varied nutrient levels on the concentration and distribution of manganese within the potato plant: Plant and Soil, vol. 6, pp. 45-60.

Bortner, C. E., 1935, Toxicity of manganese to Turkish tobacco in acid Kentucky soils: Soil Science, vol. 39, pp. 15-34.

Breazeale, E. L., McGeorge, W. T., and Breazeale, J. F., 1951, Nutrition of plants considered as an electrical phenomenon—a new approach: Soil Science, vol. 71, pp. 371-375.

Brenchley, W. E., 1936, The essential nature of certain minor elements in plant nutrition: Botan. Rev., vol. 2, pp. 173-196.

Buck, L. J., 1949, Association of plants and minerals: Jour. New York Bot. Garden, vol. 50, pp. 265-269.

Buck, L. J., 1951, Shrub aids in determining extent of orebody: Jour. New York Bot. Garden, p. 22, January-February.

Byers, R. R., 1956, Geochemical investigations: Canadian Min. Jour., vol. 77, no. 4, pp. 83-86.

Byers, Horace G., Miller, John T., Williams, K. T., and Lakin, H. W., 1938, Selenium occurrence in certain soils in the United States with a discussion of related topics: U. S. Dept. Agriculture Rept. 3, Tech. Bull. 601, 74 pp.

California Division of Mines, 1953, Geochemical prospecting: Mineral Inf. Service, vol. 6, no. 3, pp. 1-5.

Campbell, J. B., and Nowasad, F. S., 1949, 1951, Problems caused by toxic and physically active principles in plants under specific soils and climates: Specialist Conference in Agricultural Proceedings.

Cannon, Helen L., 1952, The effect of uranium-vanadium deposits on the vegetation of the Colorado plateau: Am. Jour. Sci., vol. 250, pp. 735-770.

Cannon, Helen L., 1953, Geohotanical reconnaissance near Grants, New Mexico: U. S. Geol. Survey Circ. 264.

Cannon, Helen L., and Starritt, W. H., 1956, Botanical prospecting for uranium on La Ventana Mesa, Sandoval County, New Mexico: U. S. Geol. Survey Bull. 1009-M.

Clark, O. M., 1953, Geochemical prospecting for copper at Ray, Arizona: Econ. Geology, vol. 48, p. 39.

Clarke, Frank W., 1924, Date of geochemistry: U. S. Geol. Survey Bull. 770.

Collander, R., 1941, Selective absorption of cations by higher plants: Plant Physiology, vol. 14, pp. 691-720.

Comber, Norman M., 1929, An introduction to the scientific study of the soil, Arnold and Co., London.

Cooper, J. H., and Huff, L. G., 1951, Geological investigations and geochemical prospecting experiments at Johnson, Arizona: Econ. Geology, vol. 46, p. 731.

Crooke, W. M., 1954, Effect of nickel versenate on oat plants: Nature, vol. 173, pp. 403-404.

Crooke, W. M., and Inkson, R. H. E., 1955, The relationship between nickel toxicity and major nutrient supply: Plant and Soil, vol. 6, pp. 1-15.

Davis, Gwenda N., 1941, Effect of zinc sulphate on plants: Ann. Applied Biol. 28, pp. 81-84.

Dorn, Paul, 1937, Pflanzen als Anzeichen für Erzlagerstätten: Der Biologe, vol. 6, pp. 11-13, Munich.

Drake, Mack, Vengris, Jonas, and Colhy, William G. Cation exchange capacity of plant roots: Soil Science, pp. 139-147.

Drosdoff, Matthew, 1950, Minor element content of lea tung orchards: Soil Science, vol. 70, pp. 91-98.

Durrell, Cordell, 1943, Geology of the Sierra Nevada n of Visalia, Tulare County, California: California Jour. M Geology, vol. 39, no. 2, pp. 153-168.

Elgabaly, M. M., 1950, Mechanism of zinc fixation by clays and related minerals: Soil Science, vol. 69, pp. 167-

Elgabaly, M. M., Jenny, H., and Overstreet, R., 1943, I type of clay mineral on the uptake of zinc and potassium b roots: Soil Science, vol. 55, pp. 257-263.

Elgabaly, M. M., and Wiklander, L., 1952, Effect of e capacity of clay mineral and acidoid content of plant on u sodium and calcium by excised barley and pea roots: Soil vol. 67, pp. 419-424.

Emerson, Fredrick V., 1928, Agricultural geology, John and Sons, New York.

Epstein, Emanuel, and Stout, Perry R., 1951, The micro cations iron, manganese, zinc, and copper: Their uptake b in the absorbed state: Soil Science, vol. 72, pp. 47-65.

Evans, H. J., Purvis, E. R., and Bear, F. E., 1951, Effec reaction on availability of molybdenum: Soil Science, vol. 117-124.

Ferres, H. M., 1951, Influence of light and tempera nutrient uptake and use, with particular reference to zinc: Conference on Plant and Animal Nutrition, Australia, Pro pp. 240-243.

Fetzer, Wallace G., 1946, Humic acids and true organic solvents of minerals: Econ. Geology, vol. 41, pp. 47-56.

Foster, Nicholas E., 1950, Effects of excess metals on Univ. Bristol, Ann. Rept., pp. 96-114.

Fowler, G. M., 1950, Geochemical prospecting in the Mis Valley: Min. Congress Jour., vol. 36, no. 12, p. 69.

Fujimoto, Charles K., and Sherman, Donald G., 1948, F of manganese in the soil and the manganese cycle: Soil vol. 66, pp. 131-145.

Fulton, R. B., 1950, Prospecting for zinc using semi-qua chemical analyses of soils: Econ. Geology, vol. 4, p. 654.

Goldschmidt, V. M., 1930, Occurrence of germanium in c coal products: Gesell. Wiss. Göttingen, Math.-phys. K 1 heft 3, pp. 398-401.

Goldschmidt, V. M., 1937, The principles of distribu chemical elements in minerals and rocks: Chem. Soc. (L Jour., 1937, pt. 1, pp. 655-673.

Graf, D. L., and Kerr, P. F., 1950, Trace element Santa Rita, New Mexico: Geol. Soc. America Bull., vol. 1023-1052.

Grim, Ralph E., 1953, Clay mineralogy, McGraw-Hil York.

Haas, A. R. C., 1941, The pH of soils at low moisture c Soil Science, vol. 51, pp. 17-39.

Harbaugh, J. W., 1950, Biogeochemical investigations Tri-State district: Econ. Geology, vol. 45, no. 6, pp. 548-57

Harbaugh, J. W., 1953, Geochemical prospecting al through June 1952, U. S. Geol. Survey Bull. 1000-A.

Hartsock, Lydia, and Pierce, A. P. (translators), 195 chemical and mineralogical methods of prospecting for deposits: U. S. Geol. Survey Circ. 127, 37 pp.

Hawkes, Herbert E., Jr., 1947, The Geological Survey chemical prospecting unit (abst.): Washington Acad. Sci. vol. 37, pp. 375-376.

Hawkes, Herbert E., Jr., 1948, Annotated bibliography of on geochemical prospecting for ores: U. S. Geol. Survey C 6 pp.

Hawkes, Herbert E., Jr., 1949, Geochemical prospecti ores: A progress report: Econ. Geology, vol. 44, pp. 706-712.

Hawkes, Herbert E., Jr., 1950, Geochemical prospecting f in Applied Sedimentation, P. D. Trask, ed., pp. 542-593 Wiley & Sons, Inc., New York.

Hawkes, Herbert E., Jr., and Lakin, H. W., 1949, Vestigi in surface residium associated with primary zinc ore i Tennessee: Econ. Geology, vol. 44, pp. 286-295.

Heckel, E., 1899, The presence of copper in plants a quantity they may contain: Soc. Bot. France Bull. 46, n pp. 42-43.

ström, Helmar, and Nordström, Allan, 1945, Malmletningens nuvarande ståndpunkt: Meddel Jernkontorets Gruvbyrå, , pp. 1-10.

s, E. S., 1946, Locating mineral wealth; the uses of modern ls: South African Min. and Eng. Jour., vol. 57, pt. 2, no. pp. 137-139.

nes, R. S., 1945, Determination of total copper, zinc, cobalt d in soils and soil solutions: Soil Science, vol. 50, pp. 77-84.

, L. C., 1948, A sensitive field test for heavy metals in . Econ. Geology, vol. 43, pp. 675-684.

, L. C., 1952, Abnormal copper, lead, and zinc content of soil metalliferous veins: Econ. Geology, vol. 47, pp. 517-542.

d-Karrer, A. M., 1939, Antagonism of certain elements essen- plants toward chemically related toxic elements: Plant logy, vol. 14, pp. 9-29.

aka, Y., 1940, The toxic action of copper ions on the growth plant. Pt. 1: Jour. Sci. Soil Manure, Nippon, vol. 14, pp. 3.

bson, L., and Overstreet, R., 1948, The uptake by plants of ium and some products of nuclear fission adsorbed on soil s: Soil Science, vol. 65, pp. 129-134.

oski, J. J., Preyer, R. M., and Wilson, C. H., 1942, Geoal investigation in the Tri-State zinc and lead mining dist Kansas Geol. Survey, Bull. 44, pp. 51-77.

ison, Vernon C., 1942, Adsorption and fixation of copper in sandy soils of central Florida: Soil Science, vol. 53, pp. 7.

ay, Hans, and Cowan, E. W., 1933, The utilization of ed ions by plants: Science, vol. 77, pp. 394-396.

ay, Hans, 1941, Factors of soil formation, McGraw-Hill, New

ay, Hans, and collaborators, 1951, Exploring the soils of irnia: California Div. Mines Bull. 155, pp. 9-66.

ay, Hans, and Ayers, A. D., 1939, The influence of the degree uration of soil colloids on the nutrient intake by roots: Soil ol. 48, pp. 443-459.

e, Jacob S., 1949, Pedology, Pedology Publications, New wick, New Jersey.

es, L. H. P., and Leeper, G. W., 1951, The availability of s manganese oxides to plants: Plant and Soil, vol. 3, pp. 3 . . . Available manganese oxides iu neutral and alkaline pp. 154-159.

ley, Arthur P., 1923, Soil acidity, an ecological factor: Soil e, vol. 16.

ley, Walter P., 1948, Cation exchange in soils: Am. Chem. Mono. 109, Reinhold Publishing Co.

effer, D. H., and Linz, Arthur, 1952, Molybdenum comds, Interscience Publishers, New York.

uskopf, Konrad B., 1953, Tungsten deposits of Madera, o and Tulare Counties, California: California Div. Mines, al Rept. 35, 83 pp.

lrin, S. A., 1942, The content and mobility of phosphates gating from various parent materials: Pedology (U. S. S. R.), 5-6, pp. 19-25.

oda, P. K., and Sandell, E. B., 1954, Geochemistry of molybm: Geochimica et Cosmochimica Acta, vol. 6, pp. 35-63.

in, H. W., Almond, Hy, and Ward, F. N., 1952, Compilation d tests used in geochemical prospecting by the U. S. Geologirvey: U. S. Geol. Survey Circ. 161.

in, H. W., Stevens, R. E., and Almond, Hy, 1949, Field d for the determination of zinc in soils: Econ. Geology, vol. . 296-305.

vis, A. H., 1943, The teart pastures of Somerset: II. Relation ven soil and teartness: Jour. Agr. Sci., vol. 33, pp. 55-57.

gey, Ernest, 1897, Some indications of ore deposits: Aus- n Inst. Min. Eng. Trans., vol. 4, pp. 110-122.

dgren, Waldemar, 1924, The colloidal chemistry of minerals re deposits, in Colloidal chemistry vol. II, Bogue, Robert H. or), McGraw-Hill, New York.

ering, T. S., Huff, L. C., and Almond Hy, 1950, Dispersion pper from the San Manuel copper deposit, Pinal County, ina: Econ. Geology, vol. 45, no. 6, pp. 493-514.

ering, T. S., Sokoloff, V. P., and Morris, H. T., 1948, Heavy ts in altered rock over blind ore bodies, East Tintic district, ta: Econ. Geology, vol. 43, pp. 384-399.

as, Robert E., 1948, Chemical and physical behavior of r in organic soils: Soil Science, vol. 66, pp. 119-129.

Lundblad, K., Svanberg, O., and Ekman, P., 1949, The availability and fixation of copper in Swedish soils: Plant and Soil, vol. 1, no. 4, pp. 277-302.

Lundegarth, H., 1951, Leaf analysis (translation by R. L. Mitchell), Hilgar & Watts Ltd., London.

Maliuga, D. P., 1947, On soils and plants used in the search for metals: Akad. Nauk U.S.S.R. Izv., Ser. Geol., no. 3, pp. 135-138.

Maliuga, D. P., 1951, Experimental use of soil-flora method of exploration in Transural steppe provinces: Doklady Akad. Nauk U.S.S.R., vol. 76, pp. 231-233.

Marmo, Vladi, 1953, Biogeochemical investigations in Finland: Econ. Geology, vol. 48, no. 3, pp. 211-224.

Mason, Brian, 1952, Principles of geochemistry, John Wiley and Sons, New York.

McHargue, J. S., and Roy, W. R., 1932, Mineral and nitrogen content of the leaves of some forest trees at different times in the growing season: Bot. Gaz. 94, pp. 381-393.

Mehlich, Adolf, 1942, Absorption of barium and hydroxyl ions by soils and minerals in relation to pH: Soil Science, vol. 53, pp. 115-124.

Mehlich, Adolf, and Coleman, N. T., 1952, Type of soil colloid and the mineral nutrition of plants: Advances in Agronomy, vol. 4, pp. 67-96.

Mehlich, Adolf, and Drake, M., 1955, Soil chemistry and plant nutrition, in Chemistry of the soil (F. E. Bear, ed.), Reinhold Publishing Corp., N. Y.

Merrill, George P., 1906, Rocks, rock weathering and soils, Macmillan Co., New York.

Meulen, H., 1932, Distribution of molybdenum: Nature, vol. 130, p. 966.

Mitchell, R. L., 1955, Trace elements, in Chemistry of the soil, (F. E. Bear, ed.), Reinhold Publishing Corp., N. Y., pp. 253-285.

Morris, H. T., and Lovering, T. S., 1952, Supergene and hydrothermal dispersion of heavy metals in wall rocks near ore bodies in Tintic district: Econ. Geology, vol. 47, pp. 685-716.

Mulder, E. G., 1938, Over de betekenis van koper voor de groei van planten en microorganismen, Doctoral Thesis, Agricultural University, Wageningen, Holland.

Mulder, E. G., 1954, Molybdenum in relation to growth of higher plants and micro-organisms: Plant and Soil, vol. 5, pp. 368-415.

Mulder, E. G., and Gerretsen, F. C., 1952, Soil manganese in relation to plant growth: Advances in Agronomy, vol. 4, pp. 222-272.

Newton, J. D., 1928, The selective absorption of inorganic elements by various crop plants: Soil Science, vol. 26.

Nichols, M. L., and Rogers, Lewis H., 1944, Determination of small amounts of molybdenum in plauts and soils: Industrial and Engineering Chemistry, Analytical Edition, vol. 16, pp. 137-140.

Olson, O. E., Jornlin, D. F., and Moxon, A. L., 1942, Field studies on methods for determining availability of selenium to plants: Soil Science, vol. 53, pp. 365-368.

Overstreet, R., and Jacobson, L., 1952, Mechanisms of ion absorption by roots: Ann. Rev. Plant Physiology, vol. 3, pp. 189-206.

Piper, C. S., 1944, Soil and plant analysis, Interscience Publishers, New York.

Rankama, Kalervo, 1940, On the use of the trace elements in some problems of practical geology: Soc. géol. Finlande Comptes rendus, no. 14, pp. 90-106.

Rankama, Kalervo, 1947, Some recent trends in prospecting: chemical, biogeochemical and geobotanical metbods: Min. & Met. vol. 28, pp. 282-284.

Rankama, Kalervo, and Sahama, Th., 1950, Geochemistry, Univ. Chicago Press, Chicago, Ill.

Reichen, L. E., and Lakin, H. W., 1949, Field method for determination of zinc in plants: U. S. Geol. Survey Circ. 41.

Reichen, L. E., and Ward, F. N., 1951, Field method for the determination of molybdenum in plants: U. S. Geol. Survey Circ. 124, 4 pp.

Reitemeier, R. F., 1946, Effect of moisture content on the dissolved and exchangeable ions of soils of arid regions: Soil Science, vol. 61, pp. 195-214.

Reuther, W., and Smith, P. F., 1950, A preliminary report on the relation of nitrogen, potassium and magnesium fertilization to yield, leaf composition and the incidence of zinc deficiency in oranges: Am. Soc. Hort. Sci. Proc., vol. 56, pp. 27-33.

Riddell, J. E., 1950, A technique for determination of traces of epigenetic base metals, etc.: Quebec Dept. Mines, P. R. 239.

Riddell, J. E., 1952, Anomalous copper and zinc values in trees in Holland Township, Gaspe-North County: Quebec Dept. Mines, P. R. 269.

Roberts, Ellis E., 1949, Geochemical and geobotanical prospecting for barium and copper: Uupublished Ph.D. thesis, Stanford University.

Robertson, Forbes, 1956, Geochemical prospecting by soil analyses in Montana: Montana Bur. Mines and Geol. Bull. 7, 94 pp.

Robinson, W. O., 1943, Occurrence of rare earths in plants and soils: Soil Science, vol. 56, pp. 1-6.

Robinson, W. O., and Alexander, L. T., 1953, Molybdenum content of soils: Soil Science, vol. 75, pp. 287-292.

Robinson, W. O., and Edgington, Glen, 1942, Boron content of hickory and some other trees: Soil Science, vol. 53, pp. 309-319.

Robinson, W. O., and Edgington, Glen, 1945, Minor elements in plants and some accumulator plauts: Soil Science, vol. 60, pp. 15-28.

Robinson, W. O., and Edgington, Glen, 1948, Toxic aspects of molybdenum in vegetation: Soil Science, vol. 66, p. 197.

Robinson, W. O., and Edgington, Glen, 1954, Availability of soil molybdenum as shown by the molybdenum content of many different plants: Soil Science, vol. 77, pp. 237-252.

Robinson, W. O., Edgington, G., Armiger, W. H., and Breen, A. V., 1951, Availability of molybdenum as influenced by liming: Soil Science, vol. 72, pp. 267-274.

Robinson, W. O., Lakin, H. W., and Reichen, Laura A., 1947, The zinc content of plants of the Friedensville zinc slime ponds in relation to biogeochemical prospecting: Econ. Geology, vol. 42, pp. 572-582.

Rogers, L. H., and Chih-Hwa Wu, 1948, Zinc uptake by oats as influenced by applications of lime and phosphate: Am. Soc. Agron. Jour., vol. 40, pp. 563-566.

Rudrin, S. A., 1942, The content and mobility of phosphates originating from various parent materials: Pedology (U.S.S.R.) no. 5-6, pp. 19-25.

Senftle, F. E., 1946, Relation of conductivity and total solid content of lake water to its radium content, Great Bear Lake region: Can. Min. and Met. Bull. no. 413; Can. Inst. Min. Met. Trans., vol. 49, pp. 439-446.

Shaw, E., Menzel, R. G., and Dean, L. A., 1954, Plant uptake of zinc ^{65} from soils and fertilizers in the greenhouse: Soil Science, vol. 77, pp. 205-214.

Sherman, G. D., and Harmer, P. H., 1943, The manganous-manganic equilibrium of soils: Soil Sci. Soc. America Proc., vol. 7, pp. 398-405.

Soil Survey Manual, 1951, U. S. Dept. Agriculture Handbook no. 18, Washington, D.C.

Sokoloff, V. P., 1948, Chemical prospecting for ore: Geophysics, vol. 13, p. 505.

Sokoloff, V. P., 1948, Geochemical prospecting for ore: Mines Mag., vol. 38, pp. 21-24.

Sokoloff, V. P., 1949, Geochemical prospecting methods: West Australian Min. and Commercial Rev., vol. 13, no. 12, p. 16, February 1949.

Sokoloff, V. P., and Hawkes, H. E., (translators), 1950, Selected Russian papers on geochemical prospecting for ores, U. S. Geol. Survey.

Stadnichenko, Taisiam, 1946, Modern aspects of geochemistry and their application to economic geology (abst.): Am. Mineralogist, vol. 31, no. 3-4, pp. 206-207.

Stadnichenko, Taisiam, et al., 1953, Concentration of germanium in the ash of American coals: U. S. Geol. Survey Circ. 272.

Starr, C. C., 1949, Leaf samples as an aid to prospecting for zinc: Western Miner, vol. 22, no. 1, p. 43.

Steinberg, R. A., 1941, Use of *Lemna* for nutrition studies on green plants: Jour. Agric. Res., vol. 62, pp. 423-430.

Stevens, R. E., and Lakin, H. W., 1949, The chromograph, a new analytical tool for laboratory and field use: U.S. Geol. Survey Circ. 63.

Stiles, Walter, 1946, Trace elements in plants and animals, The Macmillan Co., New York.

Stout, P. R., and Meagher, W. R., 1948, Studies of the molybdenum nutrition of plants with radioactive molybdenum: Science, vol. 108, pp. 471-473.

Stout, P. R., Meagher, W. R., Pearson, G. A., and Johnson, C. M., 1951, Molybdenum nutrition of crop plants: Plant and Soil, vol. 3, pp. 51-87.

Swedish Prospecting Company, 1939, Concerning our g ical prospecting method, (brochure), 11 pp., Malmo, Swed

Thyssen, Stephan von, 1942, Geochemical and botanic tionships in the light of applied geophysics: Beitr. ange physik, vol. 10, pp. 35-84.

Tkalich, S. M., 1938, Investigation of vegetation as a prospecting: Vest. Dal'uevastoch. Filiala Akad. Nauk stok, no. 32 (5), pp. 3-25.

Trelease, S. F., 1945, Selenium in soils, plants, and Soil Science, vol. 60, pp. 125-131.

Trelease, Sam F., and Martin, Alan L., 1936, Plan poisonous by selenium absorbed from the soil: Botanical vol. 2, pp. 373-396.

Trelles, R. A., and Amato, F. D., 1949, Arsenico, vo molibeno en algunos estratos de la Republica Argentina: Cient. Argentina 149, pp. 93-107.

Truog, Emil, 1951, Mineral nutrition in plants, Univ. W Press.

U.S. Geological Survey, 1950, Selected Russian papers chemical prospecting, U.S. Geological Survey.

U.S. Department of Agriculture, 1951, Soil Survey U.S. Dept. Agriculture Handbook 18.

Vinogradova, K. G., aud Drobkov, A. A., 1949, Possible between molybdenum deficiency and the so-called clover Akad. Nauk U.S.S.R. Dokuchaev 68, pp. 357-360.

Vogt, Thorolf, 1939, "Chemical" and "botantical" ore pro in the Roros area: K. norske vidensk, selsk. vol. 12, no. 81-84.

Vogt, Thorolf, 1942, *Viscaria alpina* (L) G. Don as plant: K. uorske vidensk. selsk. vol. 15, no. 2, pp. 5-8.

Vogt, Thorolf, 1942, Notes on the vegetation at the ore at Roros: K. norske vidensk. selsk. vol. 15, no. 6, pp. 21-2

Vogt, Thorolf, and Bergh, H., 1946, Copper content samples: K. norske vidensk. selsk. vol. 19, no. 21, pp. 76-7

Vogt, Thorolf, and Braadlie, O., 1942, Vegetation and the ore deposits at Roros: K. norske vidensk. selsk. Fo 15, no. 7, pp. 25-28.

Vogt, Thorolf, Braadlie, O., and Bergh, H., 1943, Det tion of copper, zinc, lead, manganese, and iron in plants f Roros district: K. norske vidensk. selsk. Forh., vol. 16, pp. 55-58.

Vogt, Thorolf, and Bugge, Jens, 1943, Determination o in plants from the Roros district by quantitative X-ray a K. norske vidensk. selsk. Forh., vol. 16, no. 14, pp. 51-54.

Walker, Richard B., 1948, Molybdenum deficiency in se barren soils: Science, vol. 108, pp. 473-475.

Walton, Harold F., 1953, Chelation: Scientific Americ 188, no. 6, pp. 68-76.

Ward, F. N., 1951, A field method for the determin tungsten in soils: U.S. Geol. Survey Circ. 119.

Ward, F. N., 1951a, Determination of molybdenum in s rocks: Anal. Chemistry, vol. 23, pp. 788-791.

Warren, H. V., and Delavault, R. E., 1948, Biogeoc investigations in British Columbia: Geophysics, vol. 609-624.

Warren, H. V., and Delavault, R. E., 1949, Further st biogeochemistry: Geol. Soc. America Bull., vol. 60, pp.

Warren, H. V., and Delavault, R. E., 1950, A history geochemical investigations in British Columbia: Can. In Met., vol. 43, pp. 344-350.

Warren, H. V., and Delavault, R. E., 1950a, Gold an content of some trees and some horsetails in British Co Geol. Soc. America Bull., vol. 61, pp. 123-128.

Warren, H. V., and Delavault, R. E., 1954, Variations nickel content of some Canadian trees: Royal Soc. Canada vol. 48, ser. 3, sec. 4, pp. 71-74.

Warren, H. V., and Delavault, R. E., 1955, Some biogeoc investigations in eastern Canada: Can. Min. Jour., vol. 7, pp. 43-54 . . . no. 8, pp. 58-63.

Warren, H. V., Delavault, R. E., and Fortesque, John 1955, Sampling in biogeochemistry: Geol. Soc. America, no. 2, pp. 229-238.

Warren, H. V., Delavault, R. E., and Irish, R. I., 19 geochemical researches on copper in British Columbia: Ro Canada, Trans. vol. 43, pp. 119-137.

Warren, H. V., Delavault, R. E., and Irish, R. I., 19 proved dithizone field test for heavy metals in water: Ge America Bull., vol. 62, pp. 609-618.

, H. V., Delavault, R. E., and Irish, R. I., 1952a, nical investigations in the Pacific Northwest: Geol. ica Bull., vol. 63, pp. 435-484.
, H. V., Delavault, R. E., and Irish, R. I., 1952b, y studies on the biogeochemistry of iron and manga- n. Geology, vol. 47, pp. 131-145.
, H. V., Delavault, R. E., Routley, D. G., 1953, Pre- studies of the biogeochemistry of molybdenum: Royal la, Trans. ser. 3, sec. 4, vol. 47, pp. 71-75.
H. V., and Howatson, C. H., 1947, Biogeochemical for copper and zinc: Geol. Soc. America Bull., vol. 3-820.
J. E., 1919, The ecological relation of roots: Carnegie h. pub. 286, pp. 1-128.
. S., 1953, A review of American progress in geochemical and recommendations for future British work in this . Min. and Met. Trans., vol. 62, part 7, pp. 321-348.
. S., and Millman, A. P., 1951, Heavy metals in vegeta- guide to ore: Inst. Min. Met. Trans., vol. 60, part 2, pp.

Weir, Wilbert W., 1949, Soil science, J. B. Lippincott Co., New York.

Wells, R. C., 1937, Analysis of rocks and minerals: U.S. Dept. Agriculture Bull. 878.

White, W. H., 1950, Plant anomalies related to some British Columbia ore deposits: Canada Inst. Min. Met. Bull. 459, pp. 368-371.

Williams, K. T., Lakin, H. W., and Byers, H. G., 1941, Selenium in certain soils in the United States, with a discussion of related topics, 5th report: U.S. Dept. Agriculture Tech. Bull. 758, p. 57.

Willis, L. G., and Piland, J. R., 1936, The function of copper in soils and its relation to the availability of iron and manganese: Jour. Agric. Res., vol. 52, pp. 467-476.

Worthington, Joseph E., 1955, Biogeochemical prospecting at the Shawangunk mine—a case study: Econ. Geology, vol. 50, no. 4, pp. 420-429.

Wright, J. R., Sevack, R., and Atkinson, H. J., 1955, Trace element distribution in virgin profiles representing four great soil groups: Soil Sci. Soc. America Proc., vol. 19, pp. 340-344.

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